Contents

Chapter 1: Introduction to Chemistry

Ways of Expressing Concentration

The Mole

The mole is the SI unit for the amount of substance (abbreviated mol)

Definition

- A mole is the quantity of any substance that has the same number of particles found in 12 grams of carbon-12.
- The amount of substance that contains as many elementary particles as the quantity of carbon atoms in exactly 12 g of carbon-12.

Elementary particles and Avogadro's number

Elementary particles are atoms, molecules or formula unit. One mole of substance contains 6.02×10^{23} **entities** (units or elementary particles). This number of particles is called **Avogadro's number**

- ✓ One mol of carbon -12 contains 6.02×10^{23} atoms
- ✓ One mol of H_2O contains 6.02×10^{23} molecules
- ✓ One mol of NaCl contains 6.02×10^{23} formula units

Molar Mass

The molar mass of substance is the mass per mole of its entities. Molar mass has unit of gram per mol (g. mol^{-1}), for example the molar mass of NaOH is 40g.mol^{-1}

Interconversion of moles and mass

Mass (g) = number of moles X molar mass (g. mol^{-1})

Example

How many moles of NaoH are present in 80g?

$$\text{Moles of NaoH} = \frac{80 \text{ g}}{40 \text{g.mol}^{-1}} = 2 \text{ mol}$$

Problem solving

1. Ethylene, C_2H_4, is used the preparation of plastics. What is the mass of 3.22 mol of ethylene?
2. The substance KSCN (potassium thiocyanide) is frequently used to test for an iron in solution because a distinctive red colour forms when it is added. You need to prepare 1.00 L of 0.2M KSCN solution. What mass, in grams of KSCN is needed?
3. How many moles of glucose ($C_6H_{12}O_6$) are in 45 g?

Expression of concentration in terms of molarity

Molarity

Molarity (M): expresses the concentration in terms of moles of solute per litre of solution

$$\text{Molarity} = \frac{\text{amount of substance of solute(mol)}}{\text{volume ofsolution (L)}}$$

Example

What is the molarity of solution prepared by dissolving 4.5g of NaCl in enough water to form 500 ml of solution?

Solution

(i)   Convert the mass of NaCl into moles

$$\text{Moles of solute} = \frac{\text{mass (g)}}{\text{molar mass (g.mole}^{-1})}$$

$$= \frac{4.5g}{58.5 \text{ g.mol}^{-1}} = 0.0769 \text{ mol}$$

(ii)   Convert the volume of solution into litres

$$500 \text{ ml} \times \frac{1 \text{ L}}{1000 \text{ ml}} = 0.5 \text{ L}$$

$$\text{Molarity of NaCl} = \frac{\text{Moles of solute}}{\text{volume of solution}}$$

$$= \frac{0.0769 \text{ mol}}{0.5 \text{ L}} = 0.154 \text{ mol.L}^{-1} \quad \text{or} = 0.154 \text{ M}$$

Example 2

What is the molarity of a solution prepared by dissolving 8 g of sodium hydroxide in enough water to form 200 ml of a solution?

Conversion of percent concentration to molarity

There are three different ways of representing percent concentration:

1. Percent by mass or mass-mass percent
2. Percent by volume or volume-volume percent
3. Mass-volume percent

Percent by mass (% m/m)

Percent by mass is percentage unit most often used in chemical laboratories

$$\text{Percent by mass} = \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100$$

Mass of the solution = mass of the solute + mass of solvent

$$100g = \quad 5g \quad + 95 \text{ g}$$

A solution of whose mass % concentration is 5% would contain 5g of solute per 100g

Example

What is the percent by mass of a solution containing 22g of potassium chloride, KCl, in 528g of water?

Solution

Mass of the solution = mass of the solute + mass of solvent

$$22g + 528g = 550g$$

$$\% \text{ (m/m) of KCl} = \frac{22g}{550g} \times 100g = 4 \%$$

Problem solving

Calculate percent by mass of a solution containing 20g of sodium chloride, NaCl, in 180g of water?

Percent by volume % (v/v)

Percent by volume is used in a concentration when both the solute and the solvent are either liquids or gases.

$$\text{Percent by volume} = \frac{\text{volume of solute (ml)}}{\text{volume of solution (ml)}} \times 100$$

Example

Calculate % (v/v) of 48 ml of ethanol in enough water to make 400 ml of solution

$$\text{Percent by volume} = \frac{48\ ml}{400\ ml} \times 100 = 12\ \%$$

Problem solving

350 ml of isopropyl alcohol was added water to make 500 ml isopropyl solution. Calculate % (v/v)?

Mass - volume percent (% m/v)

% (m/v) is equal to the mass of solute (in grams) divided by the total volume in (milliliters), multiplied 100

$$\text{Mass - volume percent} = \frac{\text{mass of solute (g)}}{\text{volume of solition (ml)}} \times 100$$

Thus a 2.5 % (m/v) solution of any solute contains 2.5 g of solute in each 100 ml.

Example

Calculate Mass - volume percent of 5 g NaCl dissolved in 200 ml of the solution

$$\text{Mass - volume percent} = \frac{5}{200} = 2.5\%$$

Calculating the molarity of solution expressed in percent concentration

Converting percent by mass to molarity
Example

Concentrated laboratory acid is 35 % HCl by mass and has a density of 1.18 g ml-1. What is its molarity?

Solution

1. Find the mass of 1L of solution from the density
2. Find the mass of HCl in 1L of the solution using the percent by mass
3. Convert the mass of HCl to moles of HCl

- The mass of 1L (1000 ml) of the solution is:

    1000 ml x 1.18g.ml-1 = 1180g

- Mass of HCl in 1L of the solution

    1180g x 35% = 413g

- Converting the mass of HCl to moles of HCl

$$\text{Moles of HCl} = \frac{413\ g}{36.5\ g.mol^{-1}} = 11.3\ mol$$

$$\text{Molarity} = \frac{\text{amount of solute (mol)}}{\text{Volume of solution (L)}}$$

$$\text{Molarity of HCl} = \frac{11.3\ mol}{1L} = 11.3\ mol/L\ or\ 11.3M$$

Converting mass-volume percent to molarity
Example: What is the molarity of physiological saline (0.9 % m/v) NaCl?

Solution

Since physiological saline contains 0.9g of NaCl in each 100ml of solution we can start with 100ml

$$\text{Molarity of NaCl} = \frac{\text{moles of solute}}{\text{vol of solution}} = \frac{0.9/58.5g.mol^{-1}}{0.1L} = 0.154\ mol.L^{-1}\ or\ 0.154M$$

Expression of concentration in terms of Molality

The molality of a solution, denoted m, is the moles of solute per kilogram of solvent

$$Molality\ (m) = \frac{moles\ of\ solute}{kilogram\ of\ solvent}$$

Molality of a given solution does not vary with the temperature because mass does not vary with temperature. Molarity, however, changes with temperature because the expansion or contraction of the solution changes its volume. Thus molality is often concentration unit of choice when a solution is to be used over a range of temperature.

Example

What is the molality of a solution containing 5.67g of glucose dissolved in 25.2g of water?

Solution

Convert the mass of glucose to moles

$$\frac{5.67g}{180\ g.mol\text{-}1} = 0.0315\ mol$$

Convert mass of water to kilogram

$$25.2g\ \times\ \frac{1\ kg}{1000\ g} = 0.0252\ kg$$

$$Molality = \frac{0.0315\ mol}{0.0252\ kg} = 1.25\ mol/kg\ or = 1.25m$$

Mole Fraction

The mole fraction of component A in a solution is defined as the moles of substance divided by the total moles of the solution.

$$X_A = \frac{moles\ of\ substance\ A}{total\ moles\ of\ solution}$$

The symbol X is commonly used for mole fraction, X_{HCl} = this represent the mole fraction of HCl acid

Example

What are mole fractions of glucose and water in a solution containing 5.67g of glucose, $C_6H_{12}O_6$, dissolved in 25.2g of water?

Solution

Calculating the moles of glucose:

$$\frac{5.67g}{180 \text{ g.mol-1}} = 0.0315 \text{ mol}$$

Calculating the moles of water:

$$\text{The moles of water} = \frac{25.2g}{18g.mol^{-1}} = 1.4 \text{ mol}$$

Total moles of solution = 1.4315 mol

$$X_{glucose} = \frac{0.0315 \text{ mol}}{1.4315 \text{ mol}} = 0.022 \qquad X_{water} = \frac{1.4 \text{ mol}}{1.4315 \text{ mol}} = 0.978$$

Problem solving

A solution of sodium hydroxide contains 20g of NaOH dissolved in 81g of water. Calculate

a) the mole fraction of NaOH
b) The mole fraction of water.

Conversion among concentration units

Converting molality to molarity
Example

An aqueous solution is 0.273m KCl. What is the molar concentration of potassium chloride, KCl if the density of the solution is $0.00101g.L^{-1}$ (1.011 g/ml)?

Solution

The mass of potassium chloride in this solution is:

= 0.273 mol x 74.6g.mol =20.4g

Total mass of solution =the mass of water + the mass of KCl

$$1000g + 20.4g = 1020.4g$$

$$\text{volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{1020.4g}{0.001011 \text{ g/L}} = 1.009 \text{ L}$$

$$\text{Molarity of the solution} = \frac{0.273 \text{ mol}}{1.009 \text{ L}} = 0.271 \text{ mol.L}^{-1}$$

Problem solving

What is the molar concentration of 0.322m KCl, the density of the solution is 1.011 g/mlv`r456h?

Converting Molarity to Molality
Example

An aqueous solution is 0.907M Pb $(NO_3)_3$. What is the molality of lead nitrate in this solution? The density of the solution is 1.252g.ml^{-1}.

Solution

Mass of solution = density X volume

$$1.25 \text{ X } 1000 \text{ ml} = 1252 \text{ g}$$

Mass of = 0.907 mol X 331.2 g.mol^{-1} = 300.4g

The mass of water = mass of solution – mass of lead nitrate

$$1252g - 300.4g = 952g$$

Converting the mass of water to Kg = 0.952Kg

$$\text{molality} = \frac{0.907 \text{ mol}}{0.952 \text{ Kg}} = 0.953 \text{ mol.kg}^{-1} = 0.953m$$

Names and formulas of ionic compounds

Positive ions (cations)

Monovalent Cations
Cations formed from metal atoms have the same name as the metal

Na^+ sodium ion $\qquad\qquad$ Zn^{2+} zinc ion

- Ions formed from single atoms are called monatomic ions
- monovalent atoms can only form one type of ion
- Na^+ sodium ion and Zn^{2+} zinc ion are both monovalent and monatomic ions

Multivalent Cations
If a metal can form cations of different charges, the positive charge is given by a Roman numeral in parentheses following the name of the metal

		root of Latin + ous or ic
Cu^+	Copper (I) ion	Cuprous ion
Cu^{2+}	Copper (II) ion	Cupric ion
Hg^+ or $\mathbf{Hg_2^{2+}}$	Mercury (I) ion	Mercurous ion
Hg^{2+}	Mercury (II) ion	Mercuric ion
Fe^{2+}	Iron (II) ion	Ferrous ion
Fe^{3+}	Iron (III) ion	Ferric ion
Cr^{2+}	Chromium (II) ion	Chromous ion
Cr^{3+}	Chromium (III) ion	Chromic ion
Co^{2+}	Cobalt (II) ion	Cobaltous ion
Co^{3+}	Cobalt (III) ion	Cobaltic ion
Mn^{2+}	Manganese (II) ion	Manganous ion
Mn^{3+}	Manganese (III) ion	Manganic ion
Ni^{2+}	Nickel (II) ion	Nickelous ion
Ni^{3+}	Nickel (III) ion	Nickelic ion
Pb^{2+}	Lead (II) ion	Plumbous ion
Pb^{4+}	Lead (IV) ion	Plumbic ion
Sn^{2+}	Tin (II) ion	Stannous ion
Sn^{4+}	Tin (IV) ion	Stannic ion

Negative ions (Anions)

Monatomic anions

Monatomic anions have names formed by replacing the ending of the name of the element with –ide.

H^- hydride   Oxide O^{2-} Nitride N^{3-}
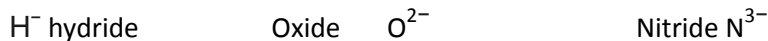
A few simple polyatomic anions also have names ending in –ide

OH^- hydroxide O_2^{2-} peroxide CN^- cyanide
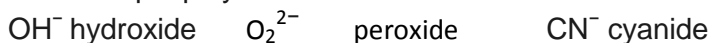
Polyatomic anions

A **polyatomic ion** is an ion that contains more than one atom.

Common Polyatomic Anions

Charge	Formula	Name
-1	$CH3COO^-$	Acetate ion
	CN^-	Cyanide ion
	OH^-	Hydroxide ion
	ClO^-	Hypochlorite ion
	ClO_2^-	Chlorite ion
	ClO_3^-	Chlorate ion
	ClO_4^-	Perchlorate ion
	NO_2^-	Nitride ion
	NO_3^-	Nitrate ion
	MnO_4^-	Permanganate
	HCO_3^-	Hydrogen carbonate (bicarbonate)
	$H_2PO_4^-$	Dihydrogen phosphate
	HSO_4^-	Hydrogen sulphate
-2	$C O_3^{2-}$	Carbonate ion
	$Cr O_4^{2-}$	Chromate ion
	$Cr_2O_4^{2-}$	dichromate ion
	$S O_3^{2-}$	Sulphite (sulfite) ion
	$S O_4^{2-}$	Sulphate(sulfate) ion
	HPO_4^{2--}	Hydrogen phosphate ion
-3	PO_4^{3-}	Phosphate ion

Oxoanions

Polyatomic anions containing one or more oxygen atoms are called oxoanions. These anions have names ending in –ite or –ate.

There are families of two or four oxoanions that differ only in the number of oxygen atoms.

Family with two Oxoanions

I.   The ions with more oxygen atoms take the nonmetal root and suffix -ate
II.   The ions with fewer oxygen atoms take the nonmetal root and suffix -ite

The ions with more oxygen		The ions with fewer oxygen atoms	
SO_4^{2-}	Sulphate(sulfate) ion	SO_3^{2-}	Sulphite (sulfite) ion
NO_3^-	Nitrate ion	NO_2^-	Nitrite ion

Family with four Oxoanions

I.   The ion with the most oxygen atoms has the prefix per-,the nonmetal root and suffix –ate
II. The ion with one fewer oxygen atom has just the nonmetal root and suffix –ate
III. The ion with two fewer oxygen atoms has just the nonmetal root and suffix –ite
IV. The ions with the least oxygen atoms has the prefix hypo-, the nonmetal root and suffix –ite

ClO_4^-	perchlorate ion	The ion with the most oxygen atoms
ClO_3^-	Chlorate ion	The ion with one fewer oxygen atom
ClO_2^-	Chlorite ion	The ion with two fewer oxygen atoms
ClO^-	Hypochlorite ion	The ions with the least oxygen atoms

Anions with the prefix hydrogen or dihydrogen

Anions derived by adding H^+ to an oxoanions are named by adding a prefix hydrogen or dihydrogen

Parent anion		Anions derived by adding H^+ to an oxoanions		Older method
CO_3^{2-}	Carbonate ion	HCO_3^-	Hydrogen carbonate	bicarbonate
SO_4^{2-}	Sulphate ion	HSO_4^-	Hydrogen sulphate	bisulfate
PO_4^{3-}	Phosphate ion	HPO_4^{2-}	Hydrogen phosphate ion	biphosphate
		$H_2PO_4^-$	Dihydrogen phosphate	

Each H^+ reduces the negative charge of the parent anion by one

Ionic compounds

Names of ionic compounds consist of the cation name followed by the anion name

KNO_3 potassium nitrate

$Cu(ClO4)_2$ copper (ii) perchlorate (cupric perchlorate)

Hydrated Compounds

Ionic compounds called hydrates have a specific number of water molecules associated with each formula unit. In their formula, this number is shown after a centered dot. It is indicated in the systematic by Greek numerical prefix before the word hydrate

Example Epsom salt has the formula $MgSO_4.7H_2O$ and the name magnesium sulfate heptahydrate.

Worked examples

1. Give the systematic names for the formulas or the formulas for the names of the following compounds a) Fe $(ClO_3)_2$ b) Ba $(OH)_2 .8H_2O$ c) Sodium sulfite

Answer

	Formula	Name
a	$Fe(ClO_3)_2$	Iron (ii) chlorate
b	$Ba(OH)_2 .8H_2O$	Barium hydroxide octahydrate
c	Na_2SO_3	Sodium sulfite

2. State why the second part of each statement is incorrect, and correct it
   a) $Ba(CH_3OO)_2$ is called barium diacetate
   b) Sodium sulfide has the formula $(Na)_2SO_3$

Answer

a) The charge of the Ba^{2+} ion must be balanced by two CH_3OO^- ions, so the prefix di- is unnecessary. The correct name is barium acetate.
b) The sodium ion is monoatomic, so it does not require parentheses. The sulfide ion is S^{2-} not SO_3^- (sulfite). The correct formula is Na_2S.

Names and the formulas of acids

The two common types of acids are binary acids and Oxoacids:

Binary acids

Binary acid solutions form when certain gaseous compounds dissolve in water for example, HCl gas forms a solution called hydrochloric acid. The name consists of the following parts
Prefix hydro- + nonmetal root + suffix -ic + acid
        Hydro   chlor   ic   acid

Name the following acids

a. H_2S
b. HI
c. HBr

Oxoacids

Oxoacids names are similar to those of the oxoanions, except for two suffix changes

i)   –ate in the anion becomes –ic in the acid

ii)   –ite in the anion becomes -ous in the acid

Anion		Corresponding acid	
ClO_4^-	perchlorate ion	$HClO_4$	Perchloric acid
ClO_3^-	Chlorate ion	$HClO_3$	Chloric acid
ClO_2^-	Chlorite ion	$HClO_2$	Chlorous acid
ClO^-	Hypochlorite ion	$HClO$	Hypochlorous acid

Name the following acids

1. H_2SO_4
2. H_2SO_3
3. HNO_3

Names and formula of binary molecular compounds

➢ Binary covalent compounds are formed by the combination of two element s, usually nonmetals

➢ Several are so familiar and we use their common names

Ammonia NH_3 Methane CH_4 Phosphine PH_3

Hydrazine N_2H_4 Water H_2O

➢ Most of binary molecular compounds in systematic way:
1. The name of the element farthest to the left in the periodic table is usually written first. The exception to this rule occurs in the case of compounds that contain oxygen.
   Oxygen is always written last except when combined with fluorine
2. If both elements are in the same group in the periodic table, the lower one is written first.
3. The second element is named with its root and the suffix –ide.
4. Greek prefixes are used to indicate the number of atoms of each element; the prefix mono- is never used with the first element.
5. When the prefix ends with in a or o and the name of second element begins with a vowel (such as oxide), the (a or o) is often dropped.

Cl_2O	dichlorine monoxide	N_2O_4	Dinitrogen tetroxide
NF_3	Nitrogen tri fluoride	P_4S_{10}	Tetra phosphorous decasulfide
CO		NO_2	
N_2O		PBr_3	
PBr_5		SF_6	

Chapter Two: Colligative Properties

A property that depends on the concentration of solute particles (molecules nor ions) , not their identity of the solute is known a Colligative property. Four of these are:

1. Vapour pressure lowering
2. Boiling point elevation
3. Freezing point depression
4. Osmotic pressure

Vapour pressure of a liquid

The vapour pressure of a liquid is the pressure of the vapour over the liquid measured at equilibrium at a given temperature.

The equilibrium of liquid and gaseous water is represented in this equilibrium:

$$H_2O \text{ (l)} \rightleftharpoons H_2O \text{ (g)}$$

The SI unit of the pressure is the Pascal (Pa) which equals a force of one Newton   exerted on an area of one square metre

$$1 \text{ Pa} = N/m^2$$

A much larger unit is the standard average atmospheric pressure measured at sea level and **0** °C

1 atm = 101,325 kPa   1 atm = 101.325 kPa

1atm = 760 mmHg   1atm = 760 torr

The vapour pressure depends on the nature of the liquid. A substance that has high vapour pressure is volatile, where as one that has no measurable vapour pressure is non-volatile.

Lowering the Vapour pressure and Raoult's Law

Raoult's law predicts that when we increase the mole fraction of non-volatile solute particles in a solution, the vapour over the solution will be reduced

Solvent alone   Solvent + solute
(a)   (b)
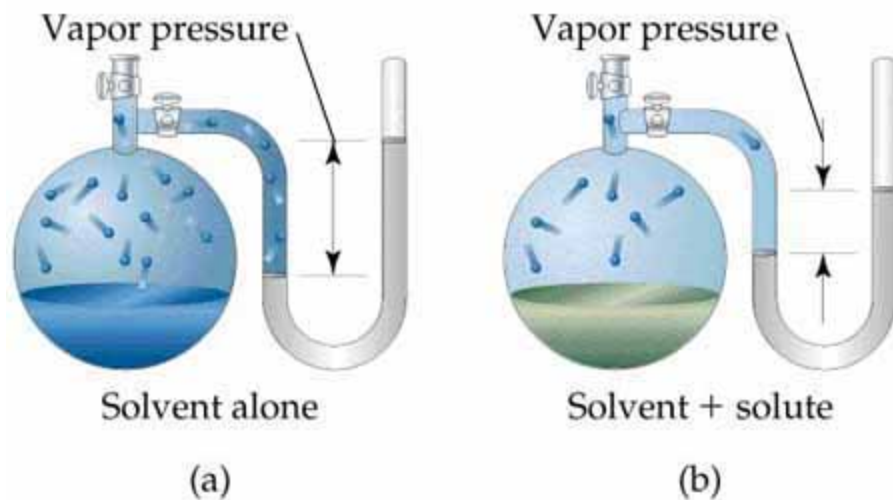
Thus, the magnitude of the vapour pressure lowering is proportional to the mole fraction of the solute in a solution.

$$\Delta P = P^0 X_{solute}$$

Vapour pressure lowering is Colligative properties which is defined as the vapour pressure over pure solvent minus the vapour pressure over the solution

$$\Delta P = P^0 - P$$

The vapour pressure over the solution =

$$P = P^0 - \Delta P$$

Or

$$P = P^0 X_{solvent}$$

where,
P   is the vapor pressure of the solution
$X_{solvent}$ is mole fraction of the solvent
P^0 is the vapor pressure of the pure solvent

X_{solute} is mole fraction of the solute

Example

Calculate the vapor pressure lowering of water when 5.67 g of glucose, $C_6H_{12}O_6$, is dissolved in 25.2 g of water at 25 °C. The vapor pressure of water at 25° C is 2.338 Kpa. What is the vapor pressure of the solution?

Solution

The molar mass of glucose ($C_6H_{12}O_6$) is 180 g.mol^{-1}, by dividing the grams of glucose by the molar mass we obtain the moles of glucose:

$$\frac{5.67g}{180g.mol^{-1}} = 0.0315 \text{ mol glucose}$$

$$\text{Moles} = \frac{\text{Mass (g)}}{\text{Molar mass(g.mol}^{-1})} = \frac{5.67g}{180 \text{ g.mol}^{-1}} = 0.0315 \text{ mol}$$

Next we find the moles of water using the grams of water, which is 25.2g

$$\text{Moles of water} = \frac{25.2g \text{ H}_2\text{O}}{18 \text{ g.mol}^{-1}} = 1.4 \text{ mol}$$

Total moles = 0.0315mol + 1.4mol =1.4315mol

Find the mole fraction of solute:

$$X_{glucose} = \frac{0.0315 \text{ mol glucose}}{1.4315 mol} = 0.022$$

Calculating the vapour pressure lowering

$\Delta P = P^0 X_{solute}$ solute: 2.338 Kpa X 0.022   =   0.0514 Kpa

Calculating the vapour pressure of the solution

$P = P^0 - \Delta P$

= 2.338 Kpa - 0.0514 Kpa = 2.2866 Kpa

Or $P = P^0 X_{solvent}$ 2.338 Kpa X 0.978 = 2.2866 Kpa

Problem Solving

1. Calculate the lowering of the vapour pressure of solution preparing by dissolving 12.4 g of non volatile solute ethylene glycol ($C_2H_6O_2$) in 68.4 g of water the vapour pressure of pure water is 17.5 torr at 20 °C?

2. Calculate the vapor pressure lowering of water when 5.67 g of glucose, $C_6H_{12}O_6$, is dissolved in 25.2 g of water at 25 °C. The vapor pressure of water at 25° C is 23.8 mmHg. What is the vapor pressure of the solution?

Boiling point elevation

Boiling point

The boiling point of liquid is the temperature at which the vapour pressure of a liquid equals 1 atm

Elevation of boiling point of the solvent

The boiling point of elevation (ΔT) is a colligative property of a solution equals to the boiling point of a solution minus the boiling point of the pure solvent.

$\Delta T_b = T_b - T_b^0$

ΔT_b is the change in boiling point of the solvent

T_b is boiling point of solution

T_b^0 is boiling point of solvent

The magnitude of the boiling point elevation is proportional to the molal concentration of the solution.

$$\Delta T_b = i\, K_b\, m$$

Where:

K_b is the **molal boiling point elevation constant**, and
m is the molal concentration of the solute in the solution

K_b of water [the boiling point of one molal solution (1 m)] = 0.512 °C/m

Or 0.512 k.kg.mol^{-1}

We can write the boiling point elevation more generally:

$$\Delta T_b = T_b - T_b^\circ = i\, K_b\, m$$

Van't Hoff Factor

i = Van't Hoff Factor

The number of particles resulting from each formula

Freezing point depression

Just as the boiling point of a solution is higher than that of pure solvent, the freezing point is lower.

$$\Delta T_f = T_f^\circ - T_f \qquad\qquad \Delta T_f = K_f m$$

We can write the boiling point elevation more generally:

$$\Delta T_f = T_f^\circ - T_f = i\, K_f\, m$$

Where:

ΔT_f is freezing point depression

T_f^0 is freezing point of the pure solvent

i = Van't Hoff Factor

K_f is the **molal freezing point depression constant**, and
m is the molal concentration of the solute in the solution

K_f of water = 1.86 k.kg.mol^{-1} or 1.86 °**C**.m^{-1}

$$\Delta T_f = i\, K_f\, m$$

Example

Automotive anti freeze consists of ethylene glycol $C_2H_6O_2$, a non volatile, non electrolyte. Calculate the boiling and freezing point of 25% by mass of the solution ethylene glycol in water.
Solution

Molar mass of $C_2H_6O_2$ = 62.1 g.mol

25 % of solution ethylene glycol contains 25g of ethylene glycol in each 100g .Thus we take 100g as the mass of solution

Mass of Solute = 25 g   Mass of water =75g

Convert mass of solute to moles

$$Moles = \frac{25g}{62.1g.mol^{-1}} = 0.4026 \; mol$$

Converting mass of water to kg

$$75 \; g \; of \; water = 75g \; X \; \frac{1 \; kg}{1000g} = 0.075kg$$

Calculating Molality

$$Molality = \frac{Moles \; of \; solute}{Solvent \; (kg)} = \frac{0.4026 \; mol}{0.075 \; kg} = 5.37 \; m$$

Calculating boiling point elevation

$$\Delta T_b = K_b m = 0.512 \; °C.m^{-1} \; x \; 5.37m = 2.7°C.$$

The boiling of solution = normal boiling point of solvent + ΔT_b

$$T_b = 100°C + 2.7°C = 102.7°C$$

Calculating the freezing point depression

$$\Delta T_f = K_f m = 1.86°C.m^{-1} \; x \; 5.37m = 10°C$$

The freezing point of solution = normal freezing point of solvent - ΔT_f

$$T_f = 0°C - 10°C = -10°C$$

Determining molality and molar mass by using ΔT_b
Example 2

A solution contains 250g of ethylene glycol dissolved in 750 g of water. The boiling point of solution was determined. It was found $\Delta T_b = 2.75°C$. Calculate:

a) The molality of the solution
b) Molar mass of the solute

Solution

Mass of ethylene glycol (solute) = 250g

Mass of solvent = 750g

$\Delta T_b = 2.75°C$

Kb of water **= 0.512°C.m^{-1}**

Calculating the molality of the solution

$$Molality = \frac{\Delta T_b}{K_b} = \frac{2.75°C}{0.512°C.m^{-1}} = 5.37m$$

Calculating the molar mass of solute

$$Molality = \frac{solute\ (g)\ /\ Molar\ mass}{Solvent\ (kg)} \qquad Molar\ mass = \frac{Solute\ (g)}{Molality\ x\ Solvent(kg)}$$

$$Molar\ mass = \frac{250g}{5.37\ mol/kg\ x\ 0.75\ kg} = 62.1\ g.mol^{-1}$$

Osmosis and Osmotic pressure

The osmotic pressure of a solution is the exert pressure needed to prevent net transport of solvent across a semipermeable membrane that separates the solution from the pure solvent. The symbol for the osmotic pressure is π (pi)

$$\pi = i\mathbf{MRT}$$

Or $\pi = cRT$

Where :

Π= osmotic pressure

i = Van't Hoff's factor

M = Molar concentration of solution (mol/L)   c= mol/L)

R = the gas constant (0.08206 L atm $mol^{-1}k^{-1}$)   or R = (kpa instead of atm) 8.314 L. $Kpa.mol^{-1}k^{-1}$)

T = temperature Kelvin (k)

Example

The formula for a low-molecular-weight starch is $(C_6H_{10}O_5)_n$, where n averages $2.00 \times 10^2 = 200$. When 0.798 g of starch is dissolved in enough water to make 100.0 mL of solution, what is the osmotic pressure of this solution at $25°C$?

Solution

 Calculate the molar mass (MM) of $(C_6H_{10}O_5)_{200}$,

  MW = (162 g/mol)(200) = 32400 g/mol

  Number of moles of starch = (0.798 g starch) / (32429 g starch / mol starch)
                = 2.46×10^{-5} mol starch

  Molarity = 2.46×10^{-5} mol/0.1 L of solution
        = 2.46×10^{-4} mol/L

Calculating osmotic pressure in Kpa

The osmotic pressure at 25 $°C$ is :

        $\pi = cRT =$ P = MRT = (2.46×10^{-4} mol/L) (8.314 L-Kpa/K-mol) (298K)

            =0.609 Kpa

Calculating osmotic pressure in atm

  P = MRT = (2.46×10^{-4} mol/L) (0.08206 L atm $mol^{-1}k^{-1}$) (298K)
  P = 6.02×10^{-3} atm
  P = 6.02×10^{-3} atm x (760 torr/atm) = 4.58 torr

Problem solving

What is the osmotic pressure at 20 ^oC of a 0.684 g of sucrose ($C_{12}H_{22}O_{11}$) per litre of the solution?

R= 8.314 L-Kpa/K-mol

Importance of osmosis in Medicine

Osmosis plays a very important role in living systems: The membrane of red blood cells is semipermeable. For intravenous feeding, it is necessary that nutrient solution must have exactly the osmotic pressure of blood plasma. If it is does not, the blood cells may collapse or burst as a result of osmosis.

Osmolarity

Osmolarity of a solution is the product of its molarity and the number of particles produced per formula unit when the solute dissociate.

Osmolarity = molarity x i

i = the number of particles produced from the dissociation of one formula unit (Van't Hoff Factor)

Example

What is the osmolarity for each of the following solution?

0.1M NaCl   = 0.1M x 2 = 0.2 **osmol**/L   or **Osm**/L

0.2 M $CaCl_2$ = 0.2M x 3 = 0.6 **Osm**/L

0.1M glucose = 0.1M x 1 = 0.1 **Osm**/L

Chapter 3 Electrolyte Solutions

An electrolyte solution is a substance that forms ions in water and conducts electricity. Acids, bases and soluble salts all produce ions in solutions, thus they all produce solutions that conduct electricity.
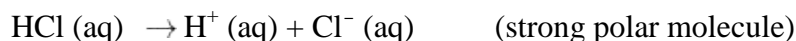
All body fluids contain electrolytes, such as:

$H_2PO_4^-$ $\quad\quad$ HCO_3^- $\quad\quad$ CO_3^{2-} $\quad\quad$ SO_4^{2-} $\quad$ Cl^- $\quad$ Na^+ $\quad$ K^+ $\quad$ Ca^{2+} $\quad$ etc
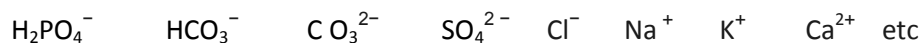
Electrolytes can be divided into groups-strong and weak electrolytes.

Strong Electrolytic Solutions

A strong electrolyte is a substance that completely (or almost completely) dissociates into ions in a solution. All strong acids, strong bases and all soluble salts are strong electrolytes. For example

$$NaCl\ (aq)\ \rightarrow Na^+\ (aq) + Cl^-\ (aq) \quad\quad \text{(ionic compound)}$$

$$HCl\ (aq)\ \rightarrow H^+\ (aq) + Cl^-\ (aq) \quad\quad \text{(strong polar molecule)}$$

Weak Electrolytic Solutions

A weak electrolyte is a substance that only partially ionizes into ions in solution .weak acids such as acetic acid, and weak bases, such as NH3, which exist in solution in large parts as unreacted molecules and only in small part as ions, behave as a weak electrolytes

$$HAc + H_2O \rightleftharpoons H_3O^+{}_{(aq)} + Ac^-{}_{(aq)}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq}$$
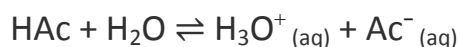
The double arrow indicates that equilibrium exists between the ions and unionized molecules of acetic acid.

More examples of strong and weak electrolytes are given below:

| Strong Electrolytes	strong acids	HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4
	strong bases	NaOH, KOH, LiOH, $Ba(OH)_2$, and $Ca(OH)_2$
	salts	NaCl, KBr, $MgCl_2$, , etc
Weak Electrolytes	weak acids	HF, $HC_2H_3O_2$ (acetic acid), H_2CO_3 (carbonic acid), H_3PO_4 (phosphoric acid), and many more
	weak bases	NH_3^+ (ammonia), C_5H_5N (pyridine

The Arrhenius Theory of acids and bases

Acids are substances which produce hydrogen ions (H) in solutions

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$
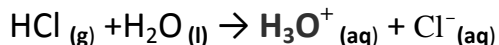
In this reaction hydrogen chloride (**HCl**) disassociates into hydrogen (**H$^+$**) and chloride (**Cl$^-$**) ions when dissolved in water.

Bases are defined as substances that release hydroxide (OH$^-$) ions into the solution.

$$NaOH_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-$$
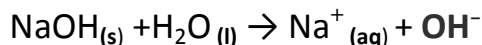
Neutralization according to Arrhenius Theory

Neutralization happens because hydrogen ions and hydroxide ions react to produce water.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$H_3O^+_{aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)}$$
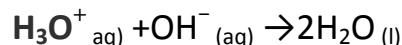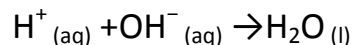
Limitation of the theory

The Arrhenius definition applies to aqueous solution, and does not describe the behavior of substances in gas phase reaction, such as formation of ammonium chloride.

$$HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)}$$
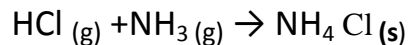
The Brønsted–Lowry Acid-Base Theory

An acid is a proton (H$^+$) donor

A base is a proton (H$^+$) acceptor

$$Acid + water \rightleftharpoons proton + conjugate\ base$$

$$HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$$

## Conjugate acid –base pairs

Conjugate (Latin): to join together

In any acid-base pair reaction, there are two conjugate acid-base pairs

- Each pair is related by the lost or gain of proton (H^+)
- One pair occurs in the forward direction
- One pair occurs in the reverse reaction

Acid + base ⇌ conjugate acid + conjugate base

With an acid, HA, the equation can be written symbolically as:
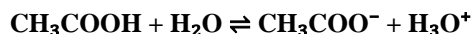
$$HA + B \rightleftharpoons HB^+ + A^-$$
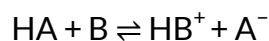
Conjugate base

The **conjugate base** of a Brønsted-Lowry is what is left after an acid has donated a proton in a chemical reaction
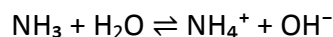
Conjugate acid

A **conjugate acid**, of a Brønsted-Lowry, is a species formed by the reception of a proton (H^+) by a base

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Acid = CH_3COOH **its conjugate base = CH_3COO^- the difference is just a proton (H^+)**

Base = H_2O **its conjugate acid = H_3O^+ the difference is just a proton (H^+)**

Water served as a base that accepts (H^+) in the above reaction. Here in the reaction of ammonia with water, Water serves as an acid that donates a proton. Thus water is amphiprotic

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

- NH_3 is a base that accepts (H^+)
- H_2O is an acid donates a proton
- NH_4^+ **conjugate acid**
- OH^- **conjugate base**

Questions
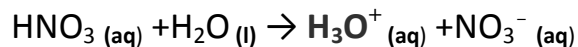
Give the formula of the conjugate base of each of the following

Acid	Conjugate base	Acid	Conjugate base
HBr		H_3O^+	
H_2S		NH_3	
H_2CO_3		HS^-	
HCO_3^-		$HClO_3^-$	
H_2O		$H_2PO_3^-$	

Give the formula of the conjugate acid of each of the following

Base	Conjugate acid	Base	Conjugate acid
H_2O		Ac^-	
NH3		NH_2	
HPO_3^{2-}		CO_3^{2-}	

Identify any Brønsted-Lowry acid base pairs

$$HNO_{3\ (aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + NO_3^-_{\ (aq)}$$

Acid	Its conjugate base	Base	Its conjugate acid

The equilibrium constant (K)

Chemical equilibrium is the state in which the reactants and the products have no net change over the time. This is when the forward and the reverse reaction occur at equal rate. This state of equilibrium can be described by the equilibrium constant (K) or Keq or Kc.

The subscript in Kc denotes that the concentration of the reactant species are expressed mol/L

The equilibrium constant, Kc can be used to find the concentration of each component of a reversible reaction at equilibrium
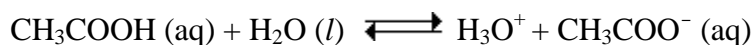
$$K_c = \frac{Product}{Reactants}$$

Example

What is the equilibrium constant expression Kc for this reaction?

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
$$\text{Reactants} \qquad \text{Products}$$
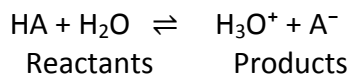
$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

What is the equilibrium constant expression Kc for this reaction?

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+ + CH_3COO^-\ (aq)$$

# Autoionization or Autoprotolysis

Autoionization is a reaction between molecules of the same substance to produce ions. It usually involves the transfer of a proton (H^+) from one molecule to the other.

The most common example is the autoionization of water:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

the interaction between water molecules is called self-ionization   or autoprotolysis

It also occurs in other substances, for example:

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
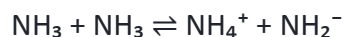
Ion product constant of water K_w

The equilibrium constant for the autoprotolysis reaction of water is:

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

Multiplying both sides of equation by $[H_2O]^2$ yields another constant (K_w).

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

K_w is ion product constant of water. This shows that the product of $[H^+] [OH^-]$ is constant in aqueous solution. At 25 °C the value of is 1.0×10^{-14}

$$(1.0 \times 10^{-7}) (1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

The acid dissociation constant K_a

The equilibrium expression for the dissociation of generic weak acid, HA in water is

$$K_c = \frac{[H_3O^+] [A^-]}{[HA] [H_2O]}$$

We simplify the equilibrium expression by multiplying kc by H_2O to define (yield) a new equilibrium constant, the acid dissociation constant, K_a.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Like any other equilibrium constant Ka is number whose magnitude is temperature dependent and tells how far to the right the reaction has proceed to reach equilibrium. The stronger acid the higher $[H_3O^+]$ and the larger K_a

The weak acids have ka value less than 1 falling mostly between 10^{-2} and 10^{-10}

The acid dissociation constant ka for some common strong and weak acids

Ka	Acid		Base	
	Name	Formula	Formula	Name
Large	Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion
$3.2 * 10^9$	Hydroiodic acid	HI	I-	Iodide
$1.0 * 10^9$	Hydrobromic acid	HBr	Br-	Bromide
$1.3 * 10^6$	Hydrochloric acid	HCl	Cl-	Chloride
$1.0 * 10^3$	Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion
$2.4 * 10^1$	Nitric acid	HNO_3	NO_3^-	Nitrate ion
1	Hydronium ion	H_3O+	H_2O	Water
$5.4 * 10^{-2}$	Oxalic acid	$HO_2C_2O_2H$	$HO_2C_2O_2^-$	Hydrogen oxalate ion
$1.3 * 10^{-2}$	Sulfurous acid	H_2SO_3	HSO_3^-	Hydrogen sulfite ion

$7.1 * 10^{-3}$	Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
$7.2 * 10^{-4}$	Nitrous acid	HNO_2	NO_3^-	Nitrite ion
$6.6 * 10^{-4}$	Hydrofluoric acid	HF	F -	Fluoride ion
$1.8 * 10^{-4}$	Methanoic acid	HCO_2H	HCO_2^-	Methanoate ion
$6.3 * 10^{-5}$	Benzoic acid	C_6H_5COOH	C_6H_5COO-	Benzoate ion

$1.8 * 10^{-5}$	Ethanoic acid	CH_3COOH	CH_3COO	Ethanoate (acetate) ion
$4.4 * 10^{-7}$	Carbonic acid	CO_3^{2-}	HCO_3^-	Hydrogen carbonate ion
$1.1 * 10^{-7}$	Hydrosulfuric acid	H_2S	HS-	Hydrogen sulfide ion

Calculation of K_a of an acid

Example

In a solution of acetic acid the equilibrium concentration are found to be

CH_3COOH = 1.OOM CH_3COO^- =0.0042M H^+ = 0.0042M

$$CH_3COOH \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons H_3O^+ + CH_3COO^- \text{ (aq)}$$

1. OOM   0.0042M.   0.0042M
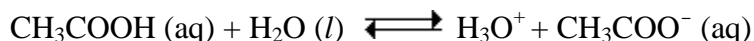
$$Ka = \frac{[H_3O][CH_3COO^-]}{[CH_3COOH]} = \frac{[0.0042]^2}{1} = 1.77 \times 10^{-5}$$

Problem Solving

0.300M of formic acid, HCOOH, has the equilibrium concentration as follow:

$$HCOOH_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

0.300M 7.35×10^{-3} 7.35×10^{-3}
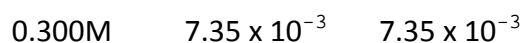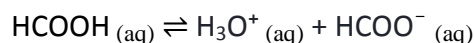
What does "p" mean?

The (p) before H^+, OH^-, K_a, K_b and Kw simply means = $-\log$

K_a	Ionization constant for acids	pk_a	Negative log of k_a = $-\log [k_a]$
K_b	Ionization constant for base	pk_b	Negative log of k_b = $-\log [k_b]$
$[H^+]$	Hydrogen ion	pH	pH=$-\log [H^+]$
OH^-	Hydroxide ion	pOH	pOH=$-\log [OH^-]$
Kw	Ion product constant of water	pKw	$-\log [Kw]=$ pKw =1×10^{14}
			$pK_w = pH + pOH$

The pH scale

The pH scale shows how acidic or basic a substance is. The pH scale ranges from **0 to 14**. A pH of 7 is neutral. A pH less than 7 is acidic. A pH greater than 7 is basic.

The pH scale is logarithmic, meaning that an increase or decrease of an integer value changes the concentration by a tenfold. For example, a pH of 3 is ten times more acidic than a pH of 4.

Likewise, a pH of 3 is one hundred times more acidic than a pH of 5. Similarly a pH of 11 is ten times more basic than a pH of 10. A pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar.

A solution can go somewhat below zero and somewhat above 14 in water, because the concentrations of hydronium ions or hydroxide ions can exceed one molar (**<0 to >14)**

Calculating the pH of Strong acids

Example

Calculate the pH of a) 0.1M HCl   b) 0.02M

Solution

Strong acids fully dissociates in water thus, 0.01M of H^+ ions

a) 0.1M HCl $= 1x\ 10^{-2}$

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

$pH = -\log [0.01]\ \ =\ -[-2]\ \ \ pH = 2$

Calculating pOH

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

Example:
calculate the pH of 0.001M NaOH.

Solution:

First find the pOH, (similar to finding the pH,) then subtract the pOH from 14.
$OH^- = 0.001M = 10^{-3}$;

$pOH = -\log [OH^-] = -\log (10^{-3}) = +3$ $pOH = 3$

$pH = 14 - pOH; pH = 14 - 3 = 11$ $pH\ \ =11$

The pH of weak acids

Monoprotic acids

When a weak acid ionizes, it gives X mol of hydrogen ion (H^+) and X mol of its conjugate base. This is summarized as follows:

ICT Table: [ion concentration at equilibrium]

Concentration(mol/L	HA	H_3O^+	A^-
Initial	1	0	0
Change	−X	+X	+X
Equilibrium	1−X	X	X

$$H^+ = X \qquad\qquad A^- = X$$

$$K_a = \frac{[x]\ [x]}{HA} \qquad\qquad K_a = \frac{X^2}{HA}$$

Example

Calculate the pH of 0.1 M of acetic acid, ka = 1.76×10^{-5}. The equation describing the ionization of acetic acid in water is:

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+ + CH_3COO^-\ (aq)$$

$$HAc\quad + H_2O \qquad \rightleftharpoons H^+{}_{(aq)} + Ac^-{}_{(aq)}$$
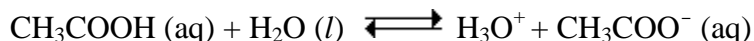
Solution

First, we can set up an ICE table for the reaction

Concentration(mol/L	HAc	H^+	Ac^-
Initial	1	0	0
Change	−X	+X	+X
Equilibrium	0.1−X	X	X

The value of this X (in 0.1-X) is very small then 0.1-X is approximately = 0.10

$$K_a = \frac{[H^+]\ [Ac^-]}{[HAc]} = 1.76 \times 10^{-5}$$

Substituting terms from the ICE table gives:

$$\frac{[x][x]}{0.10} = 1.76 \times 10^{-5} \qquad\qquad x^2 = 0.10 \times 1.76 \times 10^{-5}$$

$$x^2 = 1.76 \times 10^{-6} \qquad\qquad x = \sqrt{1.76 \times 10^{-6}}$$

$X = [H^+] = 1.33 \ 10^{-3}$ $\qquad$ pH = −log $[H^+]$ $\qquad$ pH = −log $[1.33 \ 10^{-3}]$ $\qquad$ pH = 2.88

Problem solving

Calculate the pH 0.01 M of formic acid HCOOH, Ka = 1.8×10^{-4}

Calculating the pH of a weak base

Household ammonia used for cleaning windows. What is the pH of a 3.0M solution of NH_3, K_b = 1.76×10^{-5}

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.76 \times 10^{-5} \qquad\qquad = \frac{[x][x]}{[3.0]} = 1.76 \times 10^{-5}$$

Solution

$$NH_3 \text{ (aq)} + H_2O \rightleftharpoons NH_4{}^+{}_{\text{(aq)}} + OH^-{}_{\text{(aq)}}$$
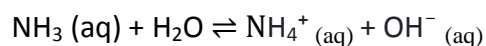
Solving for X gives: $X = [OH^-] = 7.3 \times 10^{-3}$

$$pOH = -\log [OH^-] = -\log (7.3 \times 10^{-3}) = 2.14$$

$$pH + pOH = 14 \qquad\qquad pH = 14 - 2.14$$

$$pH = 11.86$$

Polyprotic Acids

Many acids have more than one ionizable H atom. These acids are known as polyprotic acids. For example, each of the H atoms in sulfurous acid, H_2SO_3, can ionize in successive steps:

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8}$$
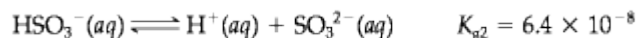
The acid-dissociation constants for these equilibria are labeled K_{a1} and K_{a2}. The numbers on the constants refer to the particular proton of the acid that is ionizing. Thus, K_{a2} always refers to the equilibrium involving removal of the second proton of a polyprotic acid. Acid –dissociation constant of some common weak polyprotic acids are shown in this table

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	

Because K_{a1} is so much larger than subsequent dissociation constants for these polyprotic acids, almost all the $H^+(aq)$ in the solution comes from the first ionization reaction. As long as successive K_a values differ by a factor of 10^3 or more, it is possible to obtain a satisfactory estimate of the pH of polyprotic acid solutions by considering only K_{a1}.

Example

What is the pH of a 0.0037 M solution of H_2CO_3?

Solution

H_2CO_3 is a diprotic acid; the two acid-dissociation constants, K_{a1} and K_{a2} differ by more than a factor of 10^3. Consequently, the pH can be determined by considering only K_{a1}, thereby treating the acid as if it were a monoprotic acid

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
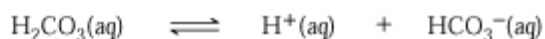
	$H_2CO_3(aq)$	$H^+(aq)$	$HCO_3^-(aq)$
Initial	0.0037 M	0	0
Change	$-x$ M	$+x$ M	$+x$ M
Equilibrium	$(0.0037 - x)$ M	x M	x M

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad \frac{(x)(x)}{0.0037} = 4.3 \times 10^{-7}$$

$$x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$$

$$x = [H^+] = [HCO_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\,M$$

$$pH = -\log[H^+] = -\log(4.0 \times 10^{-5}) = 4.40$$

Calculating concentration of conjugate base ions

If we were asked to solve for $[CO_3^{2-}]$, we would need to use K_{a2}. Let's illustrate that calculation. Using the values of $[HCO_3^-]$ and $[H^+]$ calculated above, and setting $[CO_3^{2-}] = y$, we have the following initial and equilibrium concentration values

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

	$HCO_3^-(aq)$	$H^+(aq)$	$CO_3^{2-}(aq)$
Initial	4.0×10^{-5} M	4.0×10^{-5} M	0
Change	$-y$ M	$+y$ M	$+y$ M
Equilibrium	$(4.0 \times 10^{-5} - y)$ M	$(4.0 \times 10^{-5} + y)$ M	y M

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\,M = [CO_3^{2-}]$$

Problem solving

Calculate the pH and concentration of oxalate ion, $[C_2O_4^{2-}]$, in a 0.020 M solution of oxalic acid, $H_2C_2O_4$ (see Table). ***Answers:*** pH = 1.46; $[C_2O_4^{2-}] = 6.4 \times 10^{-5}\,M$

Electron Pair Donation Theory

The Lewis Acid-Base Definition

G.N. Lewis proposed the electron pair donation theory of covalent bonding. He realized that the concept of acids and bases could be generalized to include reactions of acidic and basic oxides and many other reactions as well as proton transfer.

According to the concept:

Lewis acid: a substance that accepts an electron pair.

Lewis base: a substance that donates an electron pair.

Examples

The reaction between Na_2O and SO_3 is an example of a Lewis acid base reaction. It involves the reaction of the oxide ion, O^{2-}, from the ionic solid, Na_2O with SO_3

| Lewis base | Lewis acid | Acid-base adduct |
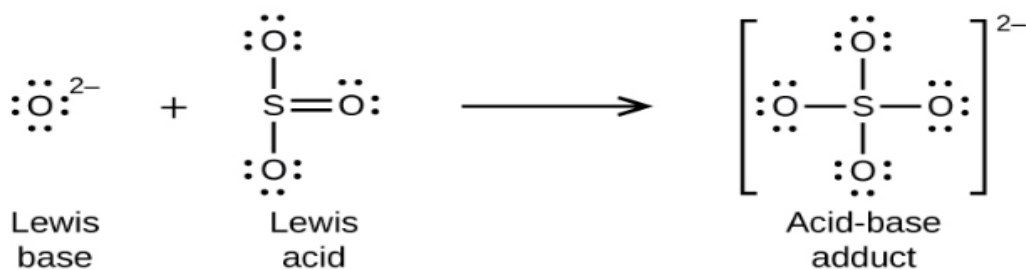
 Here SO_3 accepts the electron pair from the O^{2-} ion. At same time an electron pair from (S=O) bond moves to O^{2-} and form a **coordinate covalent bond**. Thus O^{2-} is the Lewis base SO_3 is the Lewis acid.

Coordinate covalent bond

A **coordinate covalent bond** (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.
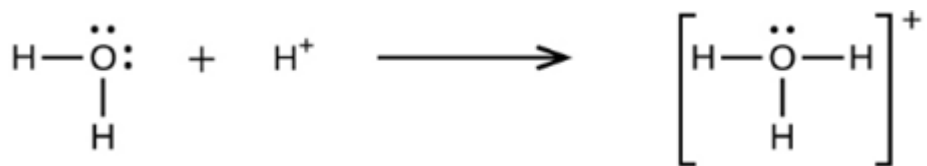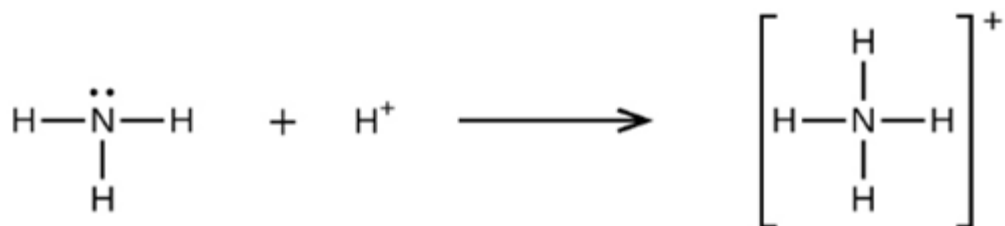
Another typical example is the reaction of the hydroxide ion with carbon dioxide to give the bicarbonate ion, as shown in Figure below. The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.
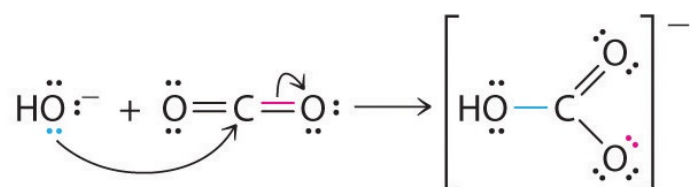
Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide

The Lewis concept embraces many reactions that we might not think of acid-base reaction. The reaction of boron trifluoride with ammonia is an example
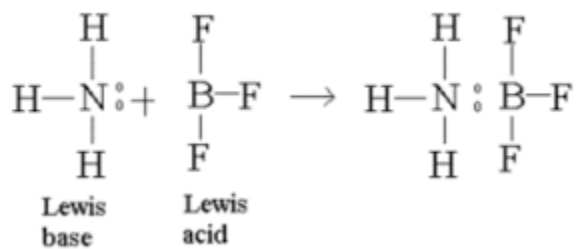
Equilibria of Slightly Soluble Ionic Compounds

The Solubility Product Constant K_{sp}

- Insoluble solids have solubility $< 0.01 M.L^{-1}$. Also often referred as slightly soluble salts
- Many natural processes depend on the precipitate or dissolving of slightly soluble salts

Kidney stones form when salts such as calcium phosphate or calcium oxalate, slowly precipitates in the kidney

Soluble	Insoluble or slightly soluble
All nitrates	none
All sodium potassium and ammonium	none
Most chlorides, bromides, and iodides	Silver and lead chloride, bromide, and iodide
Most sulphates	Calcium, lead and barium sulphates
Na^+, K^+, Rb^+, Cs^+ and NH_4^+	Most other carbonates
Na^+, K^+, Rb^+, Cs^+ and NH_4^+	Most other phosphates

Solubilty [the molar solubility, S]

the molar solubility, S is defined as the number of moles of solute in 1 L of saturated solution (moles/L)

solubility product constant , K_{sp}: it is the product of the equilibrium concentration of ions. These quantities are related, but not the same. If we know one , we can determine the other

Example

At 25 ^oC, the solubility of AgCl is 1.91×10^{-3} $g.L^{-1}$ and the molar mass of AgCl is $143.4 g.mol^{-1}$.

Calculate the solubilty product constant, $[K_{sp}]$

Solution

Convert grams per litre to mole per litre

$$\text{Molar solubility of AgCl} = \frac{1.91 \times 10^{-3} \text{ g.L}^{-1}}{143.4 \text{g.mol}^{-1}} = 1.33 \times 10^{-5} \text{ mol/L}$$

Liquid (water) and the solid (AgCl) do not include the solubility product constant $[K_{sp}]$

$K_{sp} = [Ag^+][Cl^-]$ $= 1.33 \times 10^{-5} \times 1.33 \times 10^{-5} = 1.77 \times 10^{-10}$

Example 2

Calculate the soubility of AgCl in water in grams per litre ksp = 1.77×10^{-10}

Solution

$$K_{sp} = [Ag^+][Cl^-]$$

$$1.77 \times 10^{-10} = [Ag^+][Cl^-]$$

$$[Ag^+] = [Cl^-] = \sqrt{1.77 \times 10^{-10}} = 1.33 \times 10^{-5} \text{ mol/L}$$

Problem solving

The soubility of barrium sulphate at 298 k is 1.5×10^{-5} mol/L. Calculate the solubilty product constant, $[K_{sp}]$

The equilibrium is:

$$BaSO_{4\ (s)} + \rightleftharpoons Ba^{2+}_{\ (aq)} + SO_4^{2-}_{\ (aq)}$$
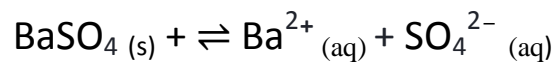
Buffer solutions

A buffer is a solution that can resist pH change upon the addition small amount of strong acid or strong base.

What is a buffer composed of?

Buffers must contain either a weak conjugate acid-base pair, meaning either a) a weak acid and its conjugate base, or b) a weak base and its conjugate acid. Thus a buffer solution is called buffer system or buffer pair.

For **example,**

- Acetic acid (weak organic acid formula CH_3COOH) and a salt containing its conjugate base, the acetate anion (CH_3COO^-), such as sodium acetate (CH_3COONa)

- Ammonia (weak base w/ formula NH_3) and a salt containing its conjugate acid, the ammonium cation, such as Ammonium chloride (NH_4Cl)

Buffer system	Conjugate acid	Conjugate base
HAc-NaAc	HAc	Ac-
$NH_4Cl - NH_3$	NH_4^+	NH_3

How buffer works

When a strong acid is added to the buffer it supplies hydrogen ions that react with the base Ac^- (an ant acid component). For example, HAc-NaAc system has the equilibrium:

$HAc \rightleftharpoons Ac^- + H_3O$

After adding a strong acid

Ac⁻ + H₃O ⇌ HAc $_{(aq)}$ + H₂O

If a strong base is added to the buffer, it supplies hydroxide that reacts with the acid (an anti-base component)

HAc $_{(aq)}$+ OH⁻ ⇌ H₂O + Ac⁻ $_{(aq)}$
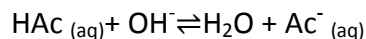
Calculating the pH of the Buffer

The Henderson-Hasselbalch equation

To calculate the pH of a buffer made up of a weak acid HA and it's conjugate base A⁻ . The acid ionization constant is:

Chemical Equilibrium: HA (aq) +   H₂0   ⇔   H+(aq) +   A-(aq)
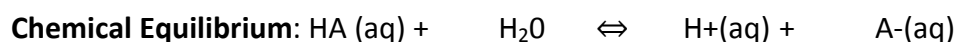
Acid Dissociation Constant k$_a$:

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

Rearranging, we get an equation for H+ concentration:

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

Take the negative logarithm of both sides:

-log (H+) = -log (ka) - log [A⁻]/ [HA]

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

For a buffer created from a base, the equation is:

$$pH = pK_b + \log \frac{[B]}{[HB^+]}$$

Example

Calculate the pH of a buffer solution made from 0.20 M $HC_2H_3O_2$ and 0.50 M $C_2H_3O_2^-$ that has an acid dissociation constant for $HC_2H_3O_2$ of 1.8 x 10^{-5}.

Solution

Solve this problem by plugging the values into the Henderson-Hasselbalch equation <u>for **a weak acid**</u> and its <u>**conjugate base**</u>.

pH = pK_a + log ([A⁻]/[HA])

pH = pK_a + log ([$C_2H_3O_2^-$] / [$HC_2H_3O_2$])

pH = -log (1.8 x 10^{-5}) + log (0.50 M / 0.20 M)

pH = -log (1.8 x 10^{-5}) + log (2.5)

pH = 4.7 + 0.40

pH = 5.1

You can calculate the pH of this buffer solution in the following equation:

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

Buffer Capacity β,

> The amount of strong acid or strong base the buffer can react before giving significant pH change

> The ability of a buffer to resist the change of potential hydrogen (pH)

> Buffering capacity is defined as the number of moles of strong base or acid needed to change the pH of a liter of buffer solution by one unit.

$$\beta = \frac{\Delta B}{\Delta pH}$$

Where, ΔB is the molar amount of the base added to the buffer

ΔpH = pH change of the buffer (pH of the buffer after adding strong base minus the pH of the buffer before addition of the strong base)

Example:

Acetate buffer contains: 0.1 moles each of acetic acid & sodium acetate in 1 liter of solution.

a) 0.01 mole portions of NaOH is added

b) The conc. of Na acetate (the [salt] in buffer equation) ↑ by 0.01 mol/l and the conc. of acetic acid [acid] ↓ by 0.01 mol/l because each increment of base converts 0.01 mole of acetic acid into 0.01 mole of sodium acetate according to the reaction.

$$\underset{(0.1 - 0.01)}{HAc} + \underset{(0.01)}{NaOH} \longleftarrow \underset{(0.1 + 0.01)}{NaAc} + H_2O$$
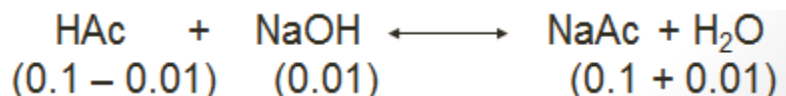
Before the addition of the first portion of NaOH, the pH of the buffer solution is

$$pH = 4.76 + \log \frac{(0.1)}{(0.1)} = 4.76$$

The changes in concentration of the salt and the acid by the addition of a base are represented in the buffer equation by using the modified form

pH = 4.76 + log (0.1 +0.01)/0.1-0.01

pH = 4.76 + log (0.11)/(0.09)

pH = 4.76 + log (1.22)

pH = 4.85

ΔpH= 4.85-4.76

ΔpH   = 0.09

Calculating the buffer capacity

$$\beta = \frac{\Delta B}{\Delta pH}$$

β = 0.01/0.09

β=0.11 mol.L^{-1}. pH^{-1}

Buffer Range

Buffer range is the pH range over which the buffer is effective and is also related to the relative buffer component concentration. The further the concentration ratio is from 1, the less effective the buffer (the less buffer capacity).

If the A/HA ratio is greater than 10 or less than 0.1 –that it is one component concentration is more than 10 times the other- buffering action is poor.

Since $\log 10 = +1$ and $\log 0.1 = -1$, *buffers have a usable range within ± 1 pH unit of the pK_a of the acid component:*

$$pH = pK_a + \log\left(\frac{10}{1}\right) = pK_a + 1 \quad \text{and} \quad pH = pK_a + \log\left(\frac{1}{10}\right) = pK_a - 1$$

Preparing a buffer

Steps of preparing a buffer solution

1. Decide on the conjugate acid –base pair (choose the acid and use sodium salts as the conjugate base).

2. Find the ratio [A⁻]/[HA] that gives the desired pH, using the Henderson-Hasselbalch equation.

3. Choose the buffer concentration and calculate the amount to mix. (Remember the higher concentration, the greater the buffer capacity. For the most laboratory application concentration from 0.5M to 0.5 M are suitable).

4. Mix the amounts together and adjust the buffer pH to the desired value. Ad small amount of acid or base, while monitoring the solution with pH meter.

Buffer's Action in Human Blood

The pH of the blood in a healthy individual remains constant at 7.35-7.45. This is because the blood contains a number of buffers that protect against pH change due to the presence of acidic or basic metabolites. From a physiological viewpoint, a change of -/+ 0.3 pH unit is extreme.

Acidosis and Alkalosis

- Acidosis is a body condition in which pH of blood drops from its normal value of 7.35 to 7.1-7.2.

- Alkalosis is the body condition in which the pH of blood increases its normal value of 7.35 to 7.5

- Both can be caused by either metabolic processes or changes in breathing.

- Metabolic acidosis is seen in diabetics, it accumulates acidic substances from the metabolism of fats. Excessive loss of bicarbonate ion in case of severe diarrhoea is another cause.

- Metabolic alkalosis is less common than metabolic acidosis. It results from elevated HCO3- ion. Causes include prolonged vomiting and Sid effect of certain drugs.

- Respiratory acidosis results from higher than normal level of CO_2 in the blood. The origin of this problem is inefficient CO_2 removal (hypoventilation) caused by lung diseases.

- Respiratory alkalosis s caused by hyperventilation (an elevated breathing rate).Causes include anxiety.

Chapter 5: Atomic structure

The Quantum Mechanics Model

Quantum mechanics describes the energy levels of an electron wave with four quantum numbers.

1	**Principal quantum number (n)**	distance from nucleus or the size of orbital
2	**Angular momentum quantum number (l)**	energy sublevel or the shape of the orbital
3	**Magnetic quantum number (m)**	Orientation in space.
4	**Spin Quantum Number, (m_s or s)**	direction of spin

Principal quantum number (n)

Describes main energy level of the electron in terms of its size or distance from the nucleus

n = 1, 2, 3, 4, 5, 6, 7

Angular momentum quantum number (l)

Angular momentum quantum number (l): Indicates the shape of orbital sublevels, l = n-1

l	0	1	2	3	4	5	...
Letter	*s*	*p*	*d*	*f*	*g*	*h*	...

The subshell with *n=2* and *l=1* is the 2*p* subshell; if *n=3* and *l=0*, it is the 3*s* subshell, and so on.

Subshell

One or more orbitals in the electron shell of an atom with the same energylevel. Subshells have different shapes and are distinguished by their magnetic quantum number

Subshell (l)	Letter Designation	orbitals	electrons
0	S	1	2
1	p	3	6
2	d	5	10
3	f	7	14
4	g	9	18

Atomic orbitals

Atomic orbitals describe where an electron is likely to be found in an atom.

An orbital in quantum number model is different from an orbit in the Bohr's model.

The orbit is a path supposedly followed by the electron, where the orbital is a mathematical function with no physical meaning

s orbitals

	$n = 1$ $\ell = 0$	
	$n = 2$ $\ell = 0$	
	$n = 3$ $\ell = 0$	

p orbitals
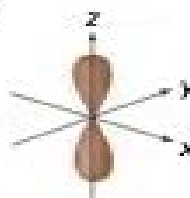
$n = 2$ $\ell = 1$
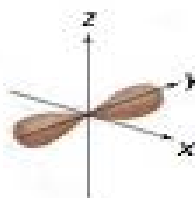
$n = 2$ $\ell = 1$
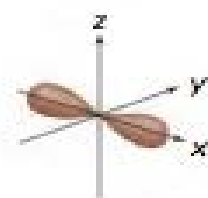
$n = 2$ $\ell = 1$

d orbitals
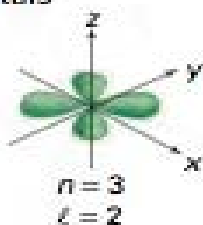
$n = 3$ $\ell = 2$
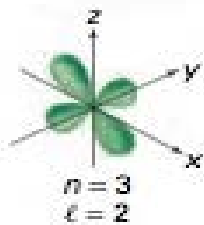
$n = 3$ $\ell = 2$
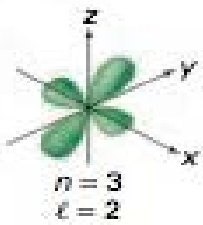
$n = 3$ $\ell = 2$
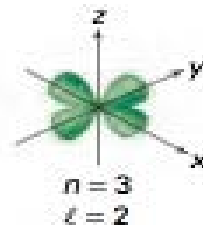
$n = 3$ $\ell = 2$
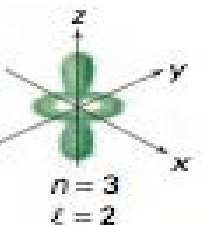
$n = 3$ $\ell = 2$

Magnetic quantum number (m)

Magnetic quantum number (m) : Indicates the orientation of the orbital in space

Values of m: integers -l to + l

The number of values represents the number of orbitals.

Example:

For l= 2, m = -2, -1, 0, +1, +2

which sublevel does this represent?   Answer: 3d

- The s orbital has one orientation

- The p sublevel can have 3 orientations

- The d sublevel can have 5 orientations

- The f sublevel can have 7 orientations.

Electron Spin Quantum Number, (m_S or s)

Spin Quantum Number, (m_S or s): Indicates the spin of the electron (clockwise or counterclockwise), or it describes the direction of spin of an electron in its orbit.

Values of m_s = +½ or -½

Electrons occur in pairs in each orbital ↑↓

Example

List the values of the four quantum numbers for orbitals in the 3d sublevel.

Answer:

n=3
l = 2
m =   -2,-1, 0, +1, +2

m_S =   +1/2, -1/2 for each pair of electrons

Table of Allowed Quantum Numbers

n	l	m_l	Number of orbitals	Orbital Name	Number of electrons
1	0	0	1	1s	2
2	0	0	1	2s	2
	1	-1, 0, +1	3	2p	6
3	0	0	1	3s	2
	1	-1, 0, +1	3	3p	6
	2	-2, -1, 0, +1, +2	5	3d	10
4	0	0	1	4s	2

The electron configuration

The electron configuration of an **atom** is the representation of the arrangement of electrons that are distributed among the orbital shells and subshells.

The spdf NOTATION

The shorthand notations of electron configuration consists: the principle energy level (n value), the letter designation of the subshell (l value) and the number of electrons in the subshell, written as superscript

For H, atomic number = 1
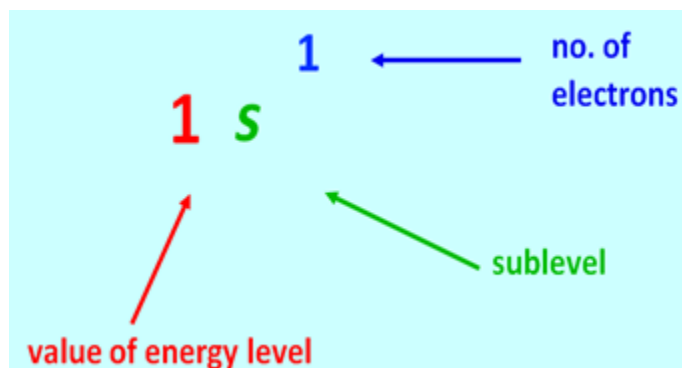
To write the electron configuration of an atom, we will first describe which energy level we are referring to and write the number of electrons in the energy level as its superscript.

Examples

	The electron configuration	
element	Complete form	Condensed electron configuration
Sulfur:	$1s^2 2s^2 2p^6 3s^2 3p^4$	$[Ne]3s^2 3p^4$

Building up principle (Aufbau's Principle)

The **Aufbau principle** states that, electrons fill the lowest available energy levels before filling higher levels (e.g., 1s before 2s)

To determine the electron configuration of the element is to start at the beginning of the periodic table.

Electrons fill the sublevels in energy order

 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

 NOTE-Some Principal Energy Levels start to fill before previous ones finish. For example 4s fills before 3d, because 4s has less energy than 3d. It must fill first.
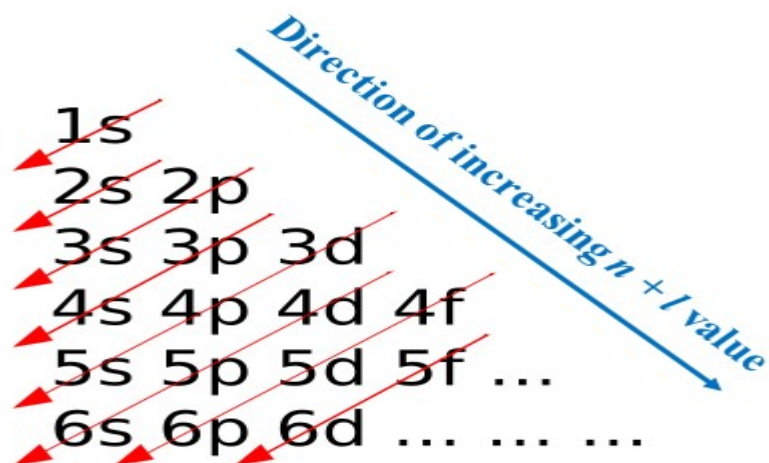
Electron configuration in the periodic table

Electron Configurations in the Perodic Table

Orbital box notation

There is another way to write electron configurations. It is called the "Box and Arrow" orbital configuration

This sublevel configuration can be broken down into orbitals (boxes).

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$$
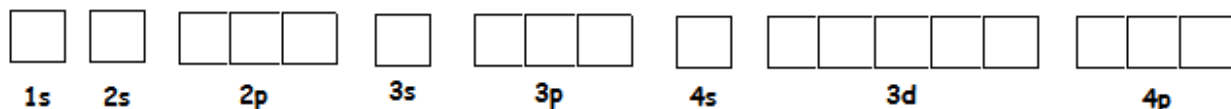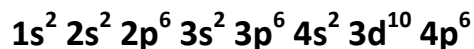
Pauli Exclusion Principle

No two electrons in the same atom can have the same four quantum numbers.

Each electron must have a unique identity as expressed by its set of quantum numbers.

An orbital can contain a maximum of 2 electrons, and they must have the opposite "spin."

Example:

Aluminum
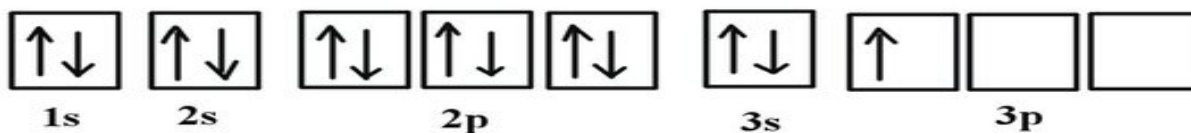
Hund's Rule

Hund's rule states that the lowest energy in a subshell is obtained by putting electrons into separate orbitals of the subshell with the same spin before pairing electrons.

Example

If we look at the correct electron configuration of **Nitrogen** (Z = 7), $1s^2\ 2s^2\ 2p^3$

Nitrogen
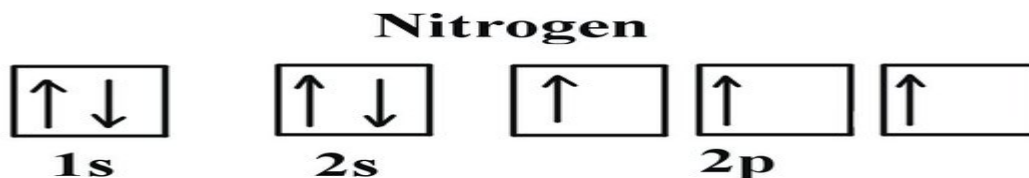
Trends in some key periodic Atomic properties

All physical and chemical behaviors of the elements are based ultimately on the electron configuration of their atoms.

Three properties of atoms that are directly influenced by electron configuration:

I.   effective nuclear charge

II.   atomic size

III.   electronegativity

Trends in effective nuclear charge

Shielding effect reduces the electrostatic attraction between the positively charged protons and the outer electrons.

Force provided by the protons is greater than the increase in repulsion due to shielding and the distance

Effective nuclear charge:

a) increases across the periodic table

b) Decrease down the group

Atomic size

Atomic size is the distance from the nucleus to the valence shell where the valence electrons are located. **Atomic size** is difficult to measure because it has no definite boundary. The electrons surrounding the nucleus exist in an electron cloud. Atomic radius is used for measuring the size of the atom.

The common atomic size include covalent radius and metallic radius

Covalent radius

Covalent radius refers to half of the distance between two nuclei of atoms joined by covalent bond

covalent radius
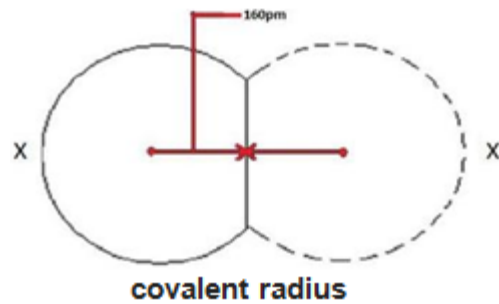
Metallic radius

The **metallic radius** is half the distance between the centers of neighboring atoms in a metal.
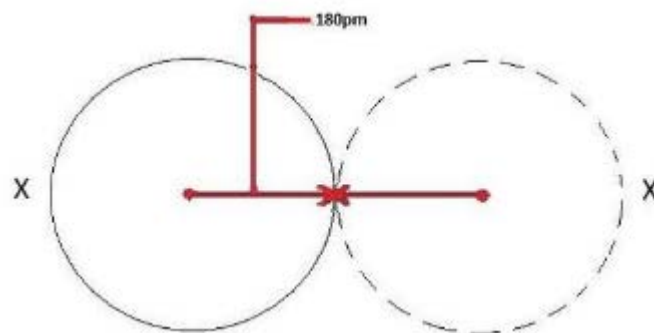
Going down a group:

▶ **The number of electron energy levels increases So, the size of the atoms increases**

Going across a period:

• **The number of protons in the nucleus increases.   The increasing nuclear charge pulls all of the electrons closer to the nucleus.**
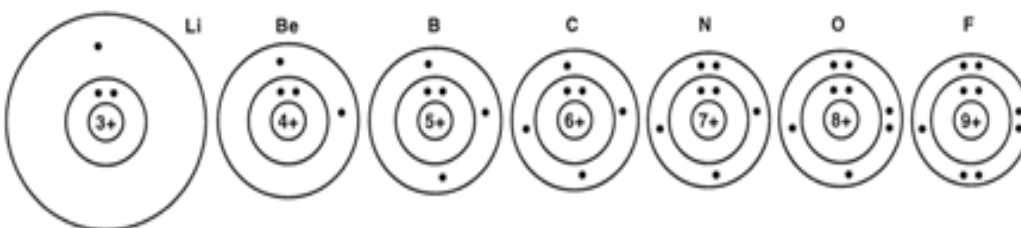
The size of the atoms decreases going across a period from left to right.
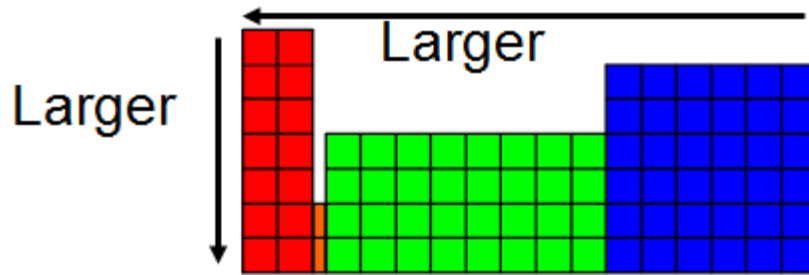
Compare the following atoms. Put in order from smallest to largest

1. Sodium, Aluminum, Potassium

2. Silver, Gold, Platinum

4. Hydrogen, Helium, Oxygen

5. Germanium, Zinc, Chromium

Trends in Electronegativity

❖ **Electronegativity** is the ability of an atom in a molecule to attract electrons to itself.

❖ The greater an atom's electronegativity is, the greater it attracts electrons to itself.

Electronegativity

❖ Increase across a period

❖ Decrease down a group

❖ Fluorine is the most electronegative element.

❖ The least electronegative element is francium

Chapter six: Molecular Structure

Chemical bonds
Chemical bonds are the attractive forces that hold atoms together.

Types of Chemical Bonds
    1) Ionic bonds 2) covalent bonds and 3) metallic bonds

Ionic bond
Ionic bond is the electrostatic force that formed between two ions by the *transfer* of electrons.
Ionic compounds usually result when metals react with nonmetals
Metals *lose* electrons to match the *number of valence electrons* of their nearest noble gas
Non-metals gain electrons from metals to achieve the octet arrangement

Covalent Bond
A covalent bond results from the sharing of electrons between   two atoms – the most familiar
of the covalent bonds are the interaction between non-metallic elements.
In 1916 G.N. Lewis proposed two atoms in a molecule are held together by a covalent bond in
which they share a pair of electrons achieving the noble gas configuration.
The Lewis structure below represents the <u>covalent bond</u> between two hydrogen atoms in a
H_2 molecule.

H : H	H−H
Dot Structure	Line Structure

Octet Rule
The tendency of toms in a molecule to have eight electrons in their valance shell is known as
the octet rule. (Hydrogen has two)

A. Types of orbital overlaps

1. Sigma bond (end to end overlap)
A Sigma (σ) is formed by the overlap of the end orbital with the end of the other. Sigma (σ)
bonds are exemplified by s-s, s-p_x and $p_x – p_x$ overlaps.

2. Pi (π) Bonds
A Pi (π) Bond is formed by the side to side overlap of two parallel p orbitals. It has and electron
distribution above and below the bond axes. pi bonds are exemplified by p_y-p_y and Pz-Pz.
A pi bond occurs after strong Sigma bond is formed.

Two atomic p orbitals	Pi (π) Bond
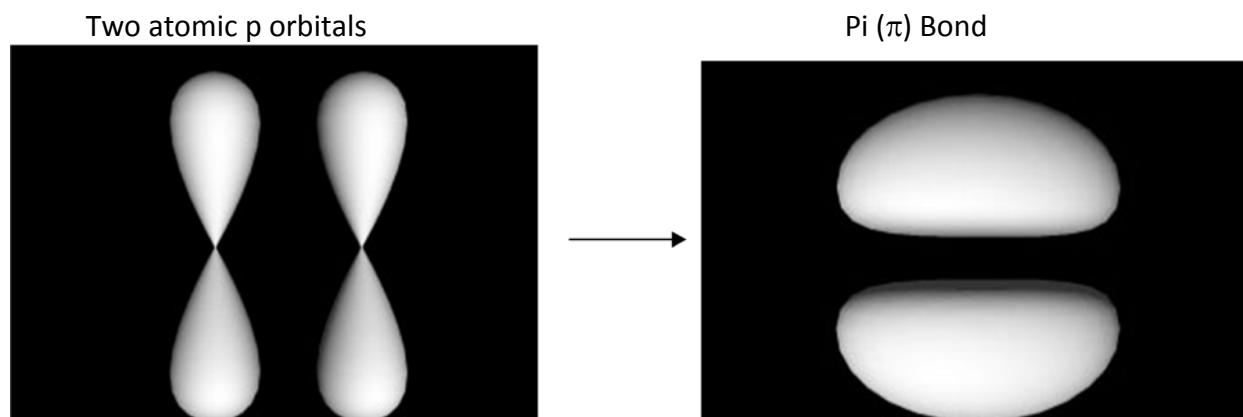
B. Types of Bonds and Bond Order

The Bond Order
The bond order is the number of electron pairs between two bonded atoms.

Single Bond
Single bond has a bond order of one. The covalent bond in H_2, HF and F_2 is a single bond that consists a single bonding pair of electrons.

Double Covalent Bond
Double bond consists of two bonding pairs, four electrons shared between two atoms, so the bond order is two. The double bond is always consists of one σ bond and one π bond. Ethylene (C_2H_4) is a simple hydrocarbon that contains a carbon – carbon double bond and four carbon hydrogen single bonds.

Triple bond
A triple bond consists of three bonding pairs, two atoms sharing six electrons, so the bond order is three. In the N_2 molecule, the atoms are held together by a triple bond, and each N atom also has lone pair electrons (a pair of electrons that does not take part the bond formation)

C) Coordinate Covalent Bond

A coordinate covalent bond is a bond in which both electrons of a shared electron pair come from one of the two atoms involved in the bond. Consider the Lewis structure of the molecule CO and NH_4^+

Dative covalent bond
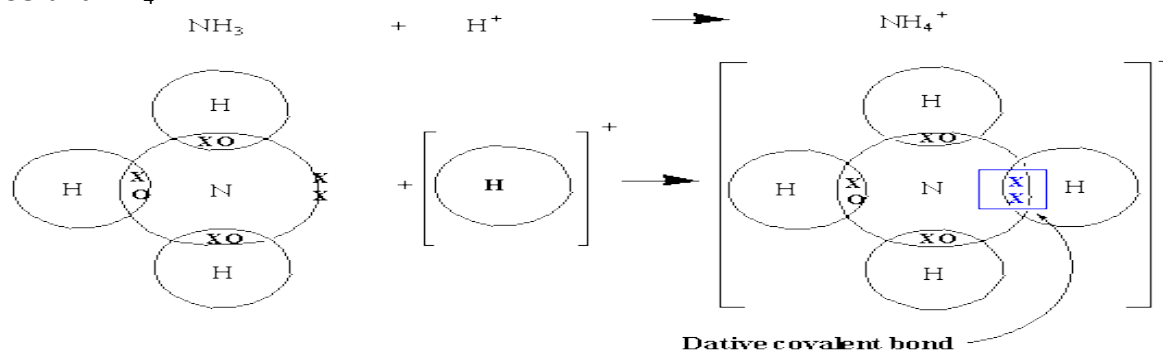
Properties of a covalent bond

Bond energy and the strength of covalent Bonds

A. Bond Energy or bond dissociation energy

It is the energy required to break one Mole of molecules into their individual atoms.

$H_{2(g)} \longrightarrow 2H_{(g)}$ $E(H-H) = D(H-H) = 436$ KJ.mol
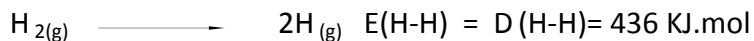
- It is the heat required to break one Mole of bonds
- **Bond energy** (**E**) is the measure of **bond strength** in a chemical bond.
- The stability of molecule is related to the strength of the covalent bonds it contains

B. Bond Length

- Bond length is defined as the distance between two nuclei of the atoms involved in the bond.
- It is determined experimentally using x-ray diffractions or the analysis of the molecular spectra.
- A close relation exists among bond order, bond length and bond energy. For example:

C-C	C=C	C≡C
154 pm	134 pm	120 pm
347 KJ.mol	614 KJ.mol	839 KJ.mol

Bond Angle

The **bond angle is the angle formed by the** nuclei of two surrounding atoms with the nucleus of the central atom at the vertex.

The bond angles of the molecule, together with the bond length, accurate define the shape of molecule.

In CCl_4 the bond angles are defied by moving a long a bond from a Cl to the central C and then to another Cl.

All Cl-C-Cl angles have the same value, 109°

Hybridization

- Hybridization occurs when atomic <u>orbitals</u> mix to form new atomic orbitals. The new orbitals have the same total <u>electron</u> capacity as the old ones.
- The process of combining atomic orbitals to give new atomic orbitals is known hybridization.

Types hybridization

A. sp Hybridization - BeF_2 (a linear shape)

The Lewis structure of beryllium fluoride is $\quad :\ddot{F}\!\!-\!\!Be\!\!-\!\!\ddot{F}:$

The orbital diagram for a ground-state Be atom is as follows:
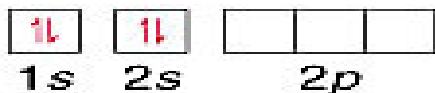
- The Be atom has no unpaired electrons.
- The Be atom in its ground state is incapable of forming bonds with the fluorine atoms.
- It can form two bonds by "promoting" one of the 2s electrons to a 2p orbital.
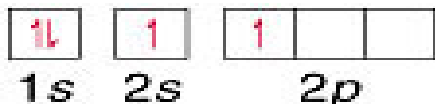
- The 2p orbital is higher energy than the 2s, this promotion requires energy.
- The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with the F atoms.
- In this case we have hybridized one s and one p orbital, so we call each hybrid an *sp hybrid orbital*.
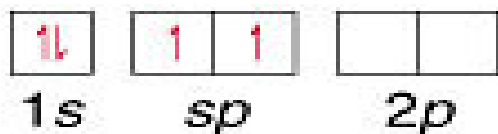
B. sp2 Hybridization- BF_3 (trigonal planar)

- in BF_3, a $2s$ electron on the B atom can be promoted to a vacant $2p$ orbital. Mixing the $2s$ and two of the $2p$ orbitals yields three equivalent sp^2 (pronounced "s-p-two") hybrid orbitals:

- The three sp^2 hybrid orbitals lie in the same plane, 120° apart from one another. They are used to make three equivalent bonds with the three fluorine atoms, leading to the trigonal planar geometry of BF_3. Notice that one of the $2p$ orbitals remains unhybridized.

C. Sp3 Hybridization - CH_4 (Tetrahedron shape)

The carbon atom in CH_4 forms four equivalent bonds with the four hydrogen atoms. We envision this process as resulting from the mixing of the $2s$ and all three $2p$ atomic orbitals of carbon to create four equivalent sp^3 (pronounced "s-p-three") hybrid orbitals:
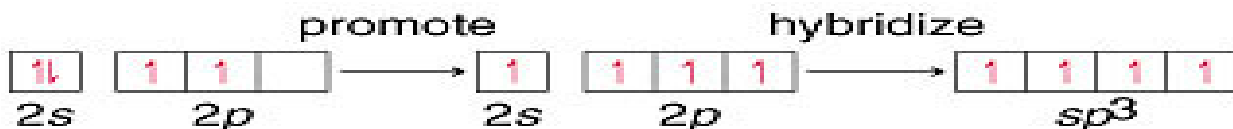
D. sp3d hybridization - PF_5 (a trigonal bipyramid shape).

Atoms in the third period and beyond can also use d orbitals to form hybrid orbitals. Mixing one s orbital, three p orbitals, and one d orbital leads to five sp^3d hybrid orbitals. The formation of sp^3d hybrids is exemplified by the phosphorus atom in PF_5:
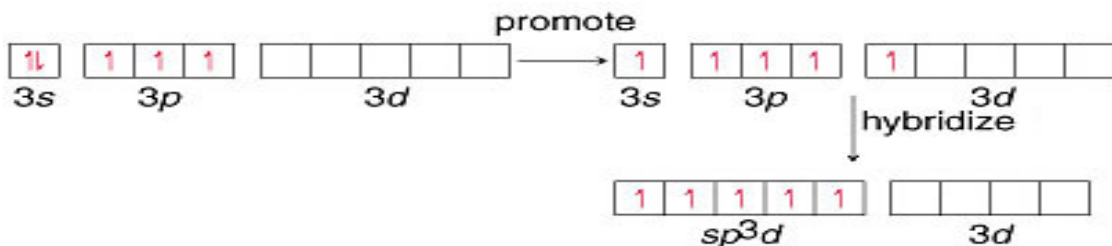
E. sp3d2 hybridization - SF_6 (octahedral Shape)

Similarly, mixing one s orbital, three p orbitals, and two d orbitals gives six sp^3d^2 hybrid orbitals, The use of d orbitals in constructing hybrid orbitals nicely corresponds to the notion of an expanded valence shell

Molecular Shapes

The shape of a molecule plays a very important role in determining its properties.

- Lewis structures tell us nothing about how atoms in a molecule are arranged in 3-dimensional space.
- By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.

VSEPR Theory

VSEPR: Valence shell electron pair repulsion

Molecules will adopt (settle) a shape that is lowest in energy
A model used to predict the geometry of molecules from the number of electron pairs surrounding their central atoms

VSEPR Notation

- In AXE notation, the "X" and the "E" may have a subscript after them to tell how many.
- Example: H_2O
  - Has 2 atoms bonded to central atom (X)
  - Has 2 lone pairs on central atom((E)
  - Its AXE notation is AX_2E_2

Determining the Molecular Geometry

1) Draw a Lewis structure
2) Count the number of bonds and lone pairs around the central atom (these are called "domains")
   - Single, Double and Triple bonds count as ONE domain
   - Each lone pair counts as ONE domain
3) Determine the shape of the molecule (use the chart).

The electron Domain
What is the electron domain?
A domain is wherever there is a <u>bond</u> or a <u>lone pair</u> around an atom

- Bonds = Bonding Domains
- Lone Pairs = Nonbonding Domains

Molecular Geometry Charts
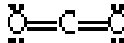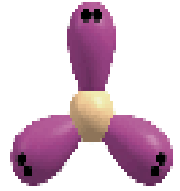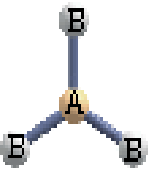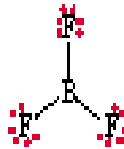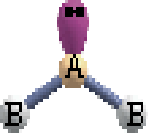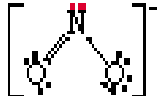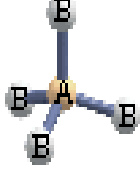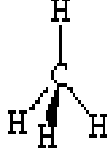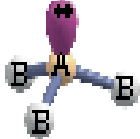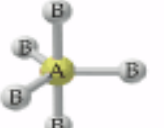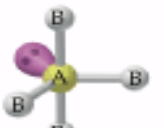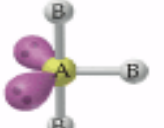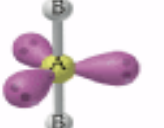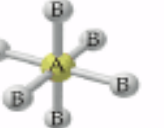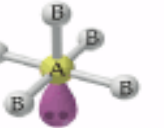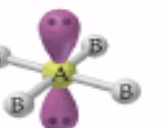
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2 domains	Linear	2	0	B—A—B Linear	$\ddot{O}=C=\ddot{O}$
3 domains	Trigonal planar	3	0	Trigonal planar	(BF₃ structure)
		2	1	Bent	(NO₂⁻ structure)
4 domains	Tetrahedral	4	0	Tetrahedral	(CH₄ structure)
		3	1	Trigonal pyramidal	(NH₃ structure)
		2	2	Bent	(H₂O structure)

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TABLE 9.3	Electron Pair Geometries and Molecular Shapes for Molecules with Five and Six Electron Pairs Domains About the Central Atom				
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5 domains	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3
		2	3	Linear	XeF_2
6 domains	Octahedral	6	0	Octahedral	SF_6
		5	1	Square pyramidal	BrF_5
		4	2	Square planar	XeF_4