

# CHEMISTRY

24 SEPTEMBER 2023

REVISION: 1687

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# 1. BASICS

## 1.1 Basics

### A. States of Matter

#### 1.1: States of Matter

- A solid has a fixed volume and a fixed shape.
- A liquid has a fixed volume, but not a fixed shape. It takes the shape of the container it is in.
- A gas has neither a fixed volume nor a fixed shape.

#### Example 1.2

Identify the states of matter of the following:

#### 1.3: Arrangement of Particles

- In a solid, particles are close together and organized.
- In a liquid, particles are close together, but disorganized.
- In a gas, particles are far apart and disorganized.

### B. Properties of Matter

#### 1.4: Physical Properties

Physical properties are characteristics a substance shows by itself, without changing into or interacting with another substance.

#### 1.5: Chemical Properties

Chemical properties are characteristics a substance shows as it changes into or interacts with another substance (or substances).

#### Example 1.6

Classify the following as physical or chemical properties

- A. color
- B. melting point
- C. electrical conductivity
- D. density
- E. flammability
- F. corrosiveness
- G. reactivity with acids

*Physical: A, B, C, D*

*Chemical: E, F, G*

#### 1.7: Physical Change

A change in physical properties of a substance is a physical change. The composition of the substance is not changed.

- All changes in states of matter are physical changes.

## 1.8: Chemical Change

- A chemical change is when the composition and properties of a substance change.
- A chemical change is more familiar as a chemical *reaction*.

### Example 1.9

Classify the following changes as chemical or physical:

- A. Melting of snow
- B. Rusting of iron
- C. Melting of sugar
- D. Caramelization of sugar

*Physical: A, C*

*Chemical: B, D*

## 1.10: Reversible versus Irreversible change

Changes that can be reversed easily are reversible.

Changes that cannot be reversed easily are irreversible.

### Example 1.11

Classify the following as reversible or irreversible. Also, classify them as physical or chemical.

- A. Breaking of glass.

## 1.12: Heating and Reversibility

Physical changes caused by heating can be reversed by cooling. But chemical changes caused by heating cannot be reversed by cooling. A more complicated series of changes is required.

## C. Length and Conversion Factors

### 1.13: Table of Prefixes

*Mega* = 1,000,000

*Kilo* = 1000

*Centi* =  $\frac{1}{100}$

*milli* =  $\frac{1}{1000}$

### 1.14: Units of Length

*1 inch* = 2.54 *cm*

*1 foot* = 12 *inches*

### Example 1.15

Optic fiber cable is sold at  $d$  dollars per foot. I need  $c$  cm. If one rupee is worth  $r$  dollars, find an expression for the cost of optic fiber cable in rupees.

#### Step by Step

Convert from cm to inches:

$$c \text{ cm} \times \frac{1 \text{ inch}}{2.54 \text{ cm}} = \frac{c}{2.54} \text{ inch}$$

Convert from inches to feet:

$$\frac{c}{2.54} \text{ inch} \times \frac{1 \text{ foot}}{12 \text{ inches}} = \frac{c}{2.54 \times 12} \text{ feet}$$

Find the cost of the cable in dollars:

$$\frac{c}{2.54 \times 12} \text{ feet} \times d \frac{\text{dollars}}{\text{foot}} = \frac{cd}{2.54 \times 12} \text{ dollars}$$

Find the conversion factor from dollars to rupees:

$$1 \text{ rupee} = r \text{ dollars} \Rightarrow 1 \text{ dollar} = \frac{1}{r} \text{ rupees} \Rightarrow 1 = \frac{1 \text{ rupees}}{r \text{ dollar}}$$

Find the cost of the cable in rupees:

$$\frac{cd}{2.54 \times 12} \text{ dollars} \times \frac{1 \text{ rupees}}{r \text{ dollar}} = \frac{cd}{r(2.54 \times 12)}$$

### Condensed Version

$$c \text{ cm} \times \frac{1 \text{ inch}}{2.54 \text{ cm}} \times \frac{1 \text{ foot}}{12 \text{ inches}} \times d \frac{\text{dollars}}{\text{foot}} \times \frac{1 \text{ rupees}}{r \text{ dollar}} = \frac{cd}{r(2.54 \times 12)}$$

## D. Scientific Notation and Volume

### 1.16: Scientific Notation

A number written in scientific notation has the form:

$$a \times 10^b$$

Where

*a has exactly one non – zero digit to the left of the decimal point*

- Scientific Notation is useful for very large and very small numbers.

### Example 1.17

Write the answers for the following in scientific notation:

- Convert 23 cm into kilometers.
- The speed of light in vacuum is approximately  $2,99,000 \frac{\text{km}}{\text{s}}$ . Write the speed of light in  $\frac{\text{cm}}{\text{s}}$ .

#### Part A

$$23 \text{ cm} = 23 \cdot \frac{1}{100} \text{ m} = \frac{23}{100} \times \frac{1}{1000} \text{ km} = \frac{2.3}{10000} \text{ km} = 2.3 \times 10^{-4} \text{ km}$$

#### Part B

$$2,99,000 \frac{\text{km}}{\text{s}} = 2.99 \times 10^5 \times 10^3 \times 10^2 \frac{\text{cm}}{\text{s}} = 2.99 \times 10^{10} \frac{\text{cm}}{\text{s}}$$

### 1.18: Units of Volume

$$\begin{aligned} 1 \text{ mL} &= 1 \text{ cm}^3 \\ 1 \text{ L} &= 1000 \text{ mL} \end{aligned}$$

### Example 1.19

An archeologist discovers a cube of dimensions  $1m \times 1m \times 1m$  made of a strange material. On tearing off a small piece, and inserting into a beaker that has water  $27\text{ mL}$ , the piece sinks, and the water level rises to  $29.1\text{ mL}$ . What proportion of the cube was torn off? Write your answer in scientific notation.

$$\frac{(29.1 - 27)\text{ cm}^3}{100 \times 100 \times 100\text{ cm}^3} = \frac{2.1}{10^6} = 2.1 \times 10^{-6} \text{ of the original cube}$$

## 1.20: Units of Mass

$$2.205\text{ pounds} = 1\text{ kg}$$

### Example 1.21

A cube of uniform density of a rare lightweight substance has mass  $2.2\text{ mg}$ . A smaller cube has edge lengths  $\frac{1}{8}$  of the larger cube. Find an expression for the mass of the smaller cube in pounds.

$$2.2 \times \underbrace{\frac{1}{1000}}_{\text{Convert to grams}} \times \underbrace{\frac{1}{1000}}_{\text{Convert to kg}} \times \underbrace{\frac{1}{8^3}}_{\text{Similarity Factor}} \times \underbrace{\frac{2.205}{10^6 \times 512}}_{\text{Convert to pounds}} \text{ pounds}$$

## E. Density

### 1.22: Fundamental Units

The base physical quantities in the SI system are:

*Mass*  
*Length*  
*Time*  
*Temperature*  
*Amount of Substance = Mole*  
*Electric Current → Amperes(A)*  
*Luminous Intensity → Candela*

### 1.23: Derived Units

Any unit which is not fundamental can be expressed in terms of fundamental units.

### 1.24: Density

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

### Example 1.25

Is density derived or fundamental?

*Derived*

### Example 1.26

## F. Temperature Scales

### 1.27: Temperature and Heat

Temperature is a measure of how hot or cold a substance is.

Heat is the *energy* that flows from a hot substance to a cold substance.

### 1.28: Temperature Scales

A method of measuring the temperature is a temperature scale.

Celsius scale has the freezing point of water at  $0^{\circ}\text{C}$ , and the boiling point of water at  $100^{\circ}\text{C}$ .

Fahrenheit scale has the freezing point of water at  $32^{\circ}\text{F}$ , and the boiling point of water at  $212^{\circ}\text{F}$ .

$$F = \frac{9}{5}C + 32$$

#### Example 1.29

- A. Convert  $50^{\circ}\text{C}$  to Fahrenheit.
- B. Find the point at which both Celsius and Fahrenheit scales have the same temperature.

#### Part A

$$F = \frac{9}{5}C + 32 = \frac{9}{5} \cdot 50 + 32 = 90 + 32 = 122^{\circ}\text{F}$$

#### Part B

When both Celsius and Fahrenheit scales have the same temperature:

$$\begin{aligned}C &= \frac{9}{5}C + 32 \\C &= -40\end{aligned}$$

### 1.30: Absolute Zero

Absolute zero temperature is the lowest temperature possible. It is  
 $-273.15^{\circ}\text{C}$

### 1.31: Kelvin Scale

The Kelvin scale sets the absolute zero temperature as its zero temperature.

$$\text{Absolute Zero} = 0\text{K} = -273.15^{\circ}\text{C}$$

$$K = C + 273.15$$

#### Example 1.32

On a linear temperature scale Y, water freezes at  $-160^{\circ}\text{Y}$  and boils at  $-50^{\circ}\text{Y}$ . On this Y scale, a temperature of  $340\text{K}$  would be read as: (JEE Main 2013, April 9)

## 1.2 Matter

### A. What is matter

#### 1.33: Elements

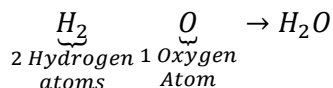
- An element is the simplest type of matter. It has unique physical and chemical properties. It consists of only one kind of atom.
- It cannot be broken down into a simpler type of matter by physical or chemical methods.

Example: Iron, oxygen, carbon

### 1.34: Compound

- Two or more different elements that are bonded *chemically*.
- The elements have a fixed ratio.

Water has two hydrogen atoms and one oxygen atom.



### Example 1.35

A compound has properties different from its elements. Explain in the context of water.

At room temperature and pressure:

*Hydrogen: Flammable Gas*  
*Oxygen: Gas*

The above two are combined to get:

*Water = H<sub>2</sub>O = Liquid*

Which has properties very different from its constituent elements.

### 1.36: Compound

Compound can be broken into simpler substances by chemical change.

For example, passing electricity through water splits it into hydrogen and oxygen.

### 1.37: Mixture

Two or more substances, which are mixed together physically, not chemically combined.

- Ratio is not fixed.
- Retains the properties of its components.
- Can be separated using physical changes

Example:

*Saltwater = Salt + Water*

## B. Some basic chemical laws

### 1.38: Law of Mass Conservation

The total mass of substances does not change during a chemical reaction.

Because  $E = mc^2$ , the mass is not exactly the same. But change in mass is very small for chemical reactions.

Law of constant composition: No matter the source, a specific compound comprises the same elements in the same ratios by mass.

### 1.39: Mass Fraction

$$\text{Mass Fraction} = \frac{\text{Mass of Element X in Compound A}}{\text{Mass of compound A}}$$



## 1.40: Mass Percent

$$\text{Mass Percent} = \text{Mass Fraction} \times 100$$

### (Calc) Example 1.41

A sample of 12 grams of phosphorus trichloride has 9.572 grams of chlorine. Find:

- A. Mass Fraction of chlorine
- B. Mass Percent of chlorine
- C. Mass of chlorine, in grams, in a metric ton of phosphorus trichloride.

#### Part A

$$\text{Mass Fraction} = \frac{\text{Mass of Chlorine}}{\text{Mass of phosphorus trichloride}} = \frac{9.572}{12} = 0.7977$$

#### Part B

$$79.77\%$$

#### Part C

$$79.77\% \times 1 \text{ ton} = 79.77\% \times 10^6 \text{ grams} = 7.977 \times 10^5$$

### (Calc) Example 1.42

The phosphorus trichloride molecule has one atom of phosphorus and three atoms of chlorine. The mass percent of chlorine in phosphorus trichloride is 79.77%. Determine mass, in grams, of phosphorus in 3 micrograms of phosphorus trichloride.

Mass percent of phosphorus

$$= 100\% - 79.77\% = 20.23\%$$

Mass of phosphorus

$$\begin{aligned} & 20.23\% \times 3 \mu\text{g} \\ &= 20.23\% \times 3 \times 10^{-6} \text{ g} \\ &= 20.23 \times 3 \times 10^{-8} \text{ g} \\ &= 60.69 \times 10^{-8} \text{ g} \\ &= 6.069 \times 10^{-7} \text{ g} \end{aligned}$$

## C. Atomic Model

Earlier, scientists used to think that the smallest component of matter was atoms. However, atoms are also divisible.

The atom consists of a small, dense, positive nucleus comprising positive protons and neutrons surrounded by negative electrons.

## 1.43 Electrons

- Electrons are negatively charged. Each electron has charge  $-1.602 \times 10^{-19} \text{ C}$ .
- They have low mass:  $9.109 \times 10^{-28} \text{ g}$
- We consider an electron to have relative charge  $-1$ .

Where

$C = \text{coloumb is the unit of charge}$

## 1.44 Plum Pudding Model

The plum pudding model proposed by Thompson had

*A spherical atom composed of diffuse, positively charged matter with electrons embedded in it like "raisins in a*

*plum pudding.”*

- When the plum pudding model was proposed, the positive particle (protons) had not been discovered.
- Hence, the model was reasonable given the information available at that time.
- Once protons were discovered, the plum pudding model was invalidated.

### 1.45 Rutherford's experiment

- Rutherford bombarded gold foil with small, dense, positively charged alpha particles.
- Most particles passed through.
- Some particles were deflected strongly.
- Particles were deflected because they encountered something positive.
- As we will learn later, alpha particles comprise two neutrons and two protons (which is identical to the nucleus of a helium atom).
- 

### Example 1.46

How did Rutherford experiment show that the plum pudding model was inaccurate?

- Positive charges repel other positive charges. If the alpha particles bounced back, then they were repelled by something positive.
- A small percentage of the particles were deflected but most passed through. This means that the deflection happened due to a small area, which contradicts the “diffuse” assumption of the plum pudding model.
- Hence, in contrast to the plum pudding model, which assumed “diffuse” positive particles, the actual positive particles were concentrated. The area in which they were concentrated is now called the nucleus.

### 1.47 Rutherford's Model

- Atom consists of small, dense, positively charged nucleus, surrounded by electrons.
- Nucleus comprises most of the mass of the atom.

### 1.48 Protons

- Protons are present in the nucleus of an atom.
- Protons are positively charged.
- Number of protons in an atom equals the number of electrons.

### Example 1.49

- A carbon atom has 6 protons. What is the number of electrons?
- Protons have a mass of  $1.672 \times 10^{-27} \text{ kg}$ . Write the mass in grams.
- What is the ratio of the mass of a proton to the mass of an electron?
- Protons have a relative charge of +1 (as compared to the electron) . What is the actual charge on the proton?

Part A

6

Part B

$1.672 \times 10^{-24} \text{ g}$

### Part C

$$\frac{1.67 \times 10^{-24} g}{9.109 \times 10^{-28} g} = \frac{1833}{1} = 1833:1$$

### Part D

$$1.602 \times 10^{-19} C$$

## 1.50 Neutrons

- Neutrons are also present in the nucleus.
- Neutrons have no charge.
- Neutrons have a mass of  $1.674 \times 10^{-24} g$ .

## Example 1.51

- What is the relative charge on a neutron?
- By what percent is the mass of a proton ( $1.672 \times 10^{-24} g$ ) greater than the mass of a neutron ( $1.674 \times 10^{-24} g$ )?

### Part A

$$0$$

### Part B

The relative mass of a neutron with respect to that of a proton is:

$$\frac{1.674 \times 10^{-24} g}{1.672 \times 10^{-24} g} = \frac{1.674}{1.672} = 1.0011$$

Hence, the mass of a neutron is greater than the mass of a proton by:

$$1.0011 - 1 = 0.0011 \text{ times} = 0.11\%$$

## D. Atomic Structure

### 1.52: Atomic Number

Atomic Number is the number of protons in the nucleus.

- All atoms of the same element have the same atomic number.
- Atomic number of one element is distinct from atomic number of any other element.

For example:

- Oxygen has atomic number 8.
- Helium has atomic number 2.

### 1.53: Mass Number

Mass Number is total number of protons and neutrons in the nucleus.

### 1.54: Atomic Symbol

The atomic symbol represents the element.

For example

$$\begin{array}{c} \text{Symbol for Carbon} = C \\ \text{Mass Number} \\ \text{Atomic Number} \end{array}$$

### Example 1.55

An atom of carbon has 12 protons and neutrons in its nucleus. It has 6 electrons. Write its atomic symbol.



### 1.56: Number of Neutrons

$$\text{Number of Neutrons} = \text{Mass Number} - \text{Atomic Number}$$

### 1.57: Isotopes

Two atoms with the same atomic number but different mass number are isotopes.

### Example 1.58

Two isotopes of carbon are  ${}^{12}_6\text{C}$  and  ${}^{14}_6\text{C}$ . Determine the number of protons, electrons and neutrons in each.

$${}^{12}_6\text{C}: 12 - 6 = 6$$

$${}^{14}_6\text{C}: 14 - 6 = 8$$

## E. Atomic Mass

### 1.59: Atomic Mass Unit

One atomic mass unit (*amu*) is  $\frac{1}{12}$  the mass of a carbon-12 atom.

### Example 1.60

*Mark all correct options*

The mass of a carbon-14 atom (in *amu*) is:

- A. Greater than 1
- B. Less than 1
- C. Equal to 1
- D. None of the above

*Option A*

### 1.61: Atomic Mass

The atomic mass of an element is the weighted average of its isotopes.

$$\text{Atomic Mass} = M_1W_1 + M_2W_2 + \cdots + M_nW_n$$

Where

$M_i$  is the mass of Isotope  $i$

$W_i$  is the relative abundance of Isotope  $i$

### Example 1.62

Carbon-12 has mass 12.00 *amu* and abundance 98.93%. Carbon-13 has mass 13.003 *amu*. Carbon-14 is the third naturally occurring isotope, but it occurs in negligible quantities. Determine the atomic mass of carbon based on this information.

$$12 \cdot 0.9893 + 13.003 \cdot (1 - 0.9893) \approx 12.01 \text{ amu}$$

### 1.63: Sum of Weights

The sum of the weights used in the calculation of atomic mass is 1.

$$W_1 + W_2 + \dots + W_n = 1$$

Use the definition of relative abundance:

$$= \frac{M_1}{\underbrace{M_1 + M_2 + \dots + M_n}_{W_1}} + \frac{M_2}{\underbrace{M_1 + M_2 + \dots + M_n}_{W_2}} + \dots + \frac{M_n}{\underbrace{M_1 + M_2 + \dots + M_n}_{W_n}}$$

Add the fractions:

$$= \frac{M_1 + M_2 + \dots + M_n}{M_1 + M_2 + \dots + M_n} = 1$$

### (No Calc) Example 1.64: Back Calculations

The atomic mass of chlorine is 35.5. Chlorine has two isotopes, chlorine-35, and chlorine-37. The ratio of these two isotopes in naturally occurring chlorine is close to: (JEE Main Sep 06 2022, Shift-II, Adapted)

#### Method I: Algebra

Let the weight of chlorine-35 be  $x$ .

Then, the weight of chlorine-37 will be  $1 - x$ .

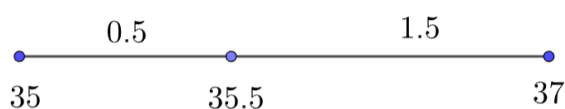
Use the formula for atomic mass:

$$35x + 37(1 - x) = 35.5$$
$$x = \frac{3}{4}, 1 - x = \frac{1}{4}$$

Ratio

$$= x : (1 - x) = \frac{3}{4} : \frac{1}{4} = 3 : 1$$

#### Method II: Shortcut



$$1.5 : 0.5 = 3 : 1$$

## 1.3 Bonding and Ions

### A. Ionic Bonding

#### 1.65: Ionic Compounds

An ionic compound typically forms when a metal transfers electrons to a nonmetal.

- The metal atom becomes a *cation* (positively charged) ion.
- The nonmetal atom becomes an *anion* (negatively charged) ion.

#### Example 1.66

Sodium chloride is an ionic compound. Identify the cation and anion.

The metal is sodium, and it will form a cation

*Sodium cation:  $\text{Na}^+$*

The chlorine is a halogen, and it will form an anion

*Chlorine anion:  $\text{Cl}^-$*

## 1.67: Ionic Crystal

- The cation and the anion in an ionic compound have opposite charges.
- These opposite charges attract due to *electrostatic* forces.
- The resulting solid array of ions is called an ionic crystal.

## 1.68: Coulomb's Law

## B. Covalent Bonding

## 1.69: Covalent Compounds

Covalent compounds are formed by sharing electrons between atoms.

2.17 - Compounds, Formulas, Names, and Masses

**Figure 2.17** Some common monatomic ions of the elements.  
Most main-group elements form one monatomic ion. Most transition elements form two monatomic ions. ( $\text{Hg}_2^{2+}$  is a diatomic ion but is included for comparison with  $\text{Hg}^{2+}$ .)

	1A (1)	2A (2)											3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	$\text{H}^+$																$\text{H}^-$	
2	$\text{Li}^+$														$\text{N}^{3-}$	$\text{O}^{2-}$	$\text{F}^-$	
3	$\text{Na}^+$	$\text{Mg}^{2+}$	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8) (9) (10)			1B (11)	2B (12)	$\text{Al}^{3+}$			$\text{S}^{2-}$	$\text{Cl}^-$	
4	$\text{K}^+$	$\text{Ca}^{2+}$				$\text{Cr}^{2+}$ $\text{Cr}^{3+}$	$\text{Mn}^{2+}$	$\text{Fe}^{2+}$ $\text{Fe}^{3+}$	$\text{Co}^{2+}$ $\text{Co}^{3+}$		$\text{Cu}^+$ $\text{Cu}^{2+}$	$\text{Zn}^{2+}$					$\text{Br}^-$	
5	$\text{Rb}^+$	$\text{Sr}^{2+}$									$\text{Ag}^+$	$\text{Cd}^{2+}$		$\text{Sn}^{2+}$ $\text{Sn}^{4+}$			$\text{I}^-$	
6	$\text{Cs}^+$	$\text{Ba}^{2+}$									$\text{Hg}_2^{2+}$ $\text{Hg}^{2+}$		$\text{Pb}^{2+}$ $\text{Pb}^{4+}$					
7																		

Table 2.3 Common Monatomic Ions*		
Charge	Formula	Name
<b>Cations</b>		
1+	H <sup>+</sup>	hydrogen
	Li <sup>+</sup>	<b>lithium</b>
	Na <sup>+</sup>	<b>sodium</b>
	K <sup>+</sup>	<b>potassium</b>
	Cs <sup>+</sup>	cesium
2+	Ag <sup>+</sup>	<b>silver</b>
	Mg <sup>2+</sup>	<b>magnesium</b>
	Ca <sup>2+</sup>	<b>calcium</b>
	Sr <sup>2+</sup>	strontium
	Ba <sup>2+</sup>	<b>barium</b>
	Zn <sup>2+</sup>	<b>zinc</b>
3+	Cd <sup>2+</sup>	cadmium
	Al <sup>3+</sup>	aluminum
<b>Anions</b>		
1−	H <sup>−</sup>	hydride
	F <sup>−</sup>	<b>fluoride</b>
	Cl <sup>−</sup>	<b>chloride</b>
	Br <sup>−</sup>	<b>bromide</b>
	I <sup>−</sup>	<b>iodide</b>
2−	O <sup>2−</sup>	<b>oxide</b>
	S <sup>2−</sup>	<b>sulfide</b>
3−	N <sup>3−</sup>	nitride

\*Listed by charge; those in **boldface** are most common.

## C. Organic Compounds

### 1.70: Organic and Inorganic Compounds

Compounds that have carbon in them are organic.

Compounds that do not have carbon in them are inorganic.

### 1.71: Alkanes

Alkanes are organic compounds with the formula:

$$C_nH_{2n+2}, n \in \mathbb{N}$$

The first few alkanes are in the table below.

**Table 3 Straight-Chain Alkane Nomenclature**

Number of carbon atoms	Name	Formula
1	methane	CH <sub>4</sub>
2	ethane	CH <sub>3</sub> —CH <sub>3</sub>
3	propane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>3</sub>
4	butane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>
5	pentane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>
6	hexane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>
7	heptane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>
8	octane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>
9	nonane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>
10	decane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>

### Example 1.72

What is the formula for pentane?



## D. Isoelectronic Ions

### 1.73: Isoelectronic

Ions that have the same number of electrons are isoelectronic.

### Example 1.74

*Mark the correct option*

$Be^{2+}$  is isoelectronic with which of the following ions?

- A.  $H^+$
- B.  $Li^+$
- C.  $Na^+$
- D.  $Mg^{2+}$  (NEET 2014)

Calculate negative charge:

$$Be^{2+}: 4 - 2 = 2$$

$$Li^+: 3 - 1 = 2$$

*Option B*

### Example 1.75

*Mark the correct option*

The ion that is isoelectronic with CO is

- A.  $N^{2+}$
- B.  $O^{2-}$



- C.  $CN^-$   
D.  $N^{2-}$  (NEET 1997)

Calculate negative charge:

$$CO: 6 + 8 = 14$$
$$CN^-: 6 + 7 + 1 = 14$$

Option C

### Example 1.76

Mark the correct option

Isoelectronic species are

- A.  $CO^-$ ,  $CN$ ,  $NO$ ,  $C^{2-}$   
B.  $CO^+$ ,  $CN^+$ ,  $NO^-$ ,  $C_2$   
C.  $CO$ ,  $CN$ ,  $NO$ ,  $C_2$   
D.  $CO$ ,  $CN^-$ ,  $NO^+$ ,  $C_2^{2-}$  (NEET 2000)

$$CO: 6 + 8 = 14$$
$$CN^-: 6 + 7 + 1 = 14$$
$$NO^+: 7 + 8 - 1 = 14$$
$$C_2^{2-}: 6 + 6 + 2 = 14$$

Option D

### Example 1.77

Which one of the following is not isoelectronic with  $O^{2-}$ ?

- A.  $Tl^+$   
B.  $Na^+$   
C.  $N^{3-}$   
D.  $F^-$  (NEET 1994)

$$O^{2-}: 8 + 2 = 10$$
$$Na^+: 11 - 1 = 10$$
$$N^{3-}: 7 + 3 = 10$$
$$F^-: 9 + 1 = 10$$
$$Tl^+ (\text{Thallium}): 81 - 1 = 80$$

Option A

## 1.4 Stoichiometry

### A. Mole

#### 1.78: Mole

One mole contains  $6.022 \times 10^{23}$  entities.

- The mole is called Avogadro's number.
- It is the number of atoms in 12g of carbon – 12.

#### 1.79: Avogadro's Number

For notation, we can write Avogadro's number as

$$N_a = 6.022 \times 10^{23}$$

### 1.80: Amu vs grams

The mass in amu of a molecule (or a formula unit) is the same as the mass in one grams of one mole of the same substance.

#### Example 1.81

Oxygen has a mass of 16 amu. Determine the number of atoms in 8 grams of oxygen.

$$0.5N_a$$

### 1.82: Molar Mass

Molar mass of a substance is the mass of one mole of its entities. Entities can be:

- Atoms
- Molecules
- Formula Unit

$$\text{Molar mass} = \frac{\text{grams}}{\text{mole}} \text{ of a substance}$$

#### Example 1.83

Determine the molar mass of

- A. sodium chloride
- B. water

$$\text{Sodium Chloride: } Na + Cl = 23 + 35.45 = 58.45$$

$$\text{Water: } H_2O \rightarrow 2(1) + 16 = 18$$

#### Example 1.84

Determine the ratio of the molar mass of a diatomic oxygen molecule to the molar mass of water.

$$32:18 = 16:9$$

#### Example 1.85

Determine the molar mass of basic zinc carbonate which has the formula  $Zn_5(CO_3)_2(OH)_6$ .

$$5Zn + 2C + 12O + 6H = 5(65.38) + 2(12.011) + 12(15.999) + 6(1.008) = 548.9$$

## B. Conversions

#### Example 1.86

The amount of oxygen, in grams, in 3.6 grams of water is:

$$3.6 \times \frac{16}{18} = 3.2 \text{ g}$$

#### Example 1.87

The amount of oxygen, in grams, in 3.6 moles of water is: (JEE Main, 9 April 2014)

Note that:

$$3.6 \text{ moles } H_2O = 3.6 \text{ moles } O, 7.2 \text{ moles } H$$

And the mass of oxygen is:

$$3.6 \text{ moles} \times 16 \frac{g}{\text{mole}} = 57.6 g$$

### Example 1.88

You have 0.125 moles of water.

- A. Determine the weight in kg
- B. Determine the number of atoms of hydrogen.

#### Part A

$$\frac{1}{8} \times 18 \times \frac{1}{1000} = \frac{9}{2} \times 10^{-3} = 4.5 \times 10^{-3} kg$$

#### Part B

$$\begin{aligned} \text{No. of water molecules} &= 0.125 N_a \\ \text{No. of hydrogen atoms} &= 2 \times 0.125 N_a = 0.25 N_a \end{aligned}$$

### Example 1.89

Determine the ratio of carbon atoms to hydrogen atoms to oxygen atoms in 3.14 moles of glucose, which has chemical formula  $C_6H_{12}O_6$ .

Number of moles is irrelevant. We only need the ratio in the formula for oxygen:

$$\text{Carbon: Hydrogen: Oxygen} = 6: 12: 6 = 1: 2: 1$$

## C. Mass Fraction and Mass Percent

### 1.90: Percentage Composition

#### Example 1.91

The percentage composition of carbon by mole in methane is: (JEE Main, April 8 2019, Shift-II)

Instead of working with one mole, we can work with a single molecule, and the answer will be the same. Hence, the "by mole" is not relevant here.

The question then becomes, "What percent of the atoms in a molecule of methane are carbon?"



Total = 1 carbon + 4 hydrogen = 5 atoms

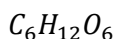
Percentage of carbon

$$= \frac{1}{5} = 20\%$$

### 1.92: Mass Fraction and Mass Percent

#### Example 1.93

Determine the mass fraction and mass percentage of the element with the highest mass percent in glucose.



$$= \frac{6(16)}{6(12) + 12(1) + 6(16)} = \frac{96}{180} = \frac{8}{15} = 53.33\%$$

#### Example 1.94

Determine the mass of oxygen in 1 gram of ferrous oxide.

$$1 \times \frac{16}{72} = \frac{2}{9} g$$

#### Example 1.95

Determine the original mass of an iron nail that rusted completely to give 10 g of rust. Assume the rust is entirely ferrous oxide.

$$10 \times \frac{56}{72} = 10 \times \frac{7}{9}$$

### D. Formulas

#### 1.96: Types of Formulas

Empirical formula shows the relative ratio of atoms of each element in a compound.

Molecular formula shows actual number of atoms of each element in a compound.

Structural formula shows relative placement and connection of atoms in a molecule.

#### Example 1.97

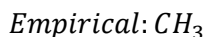
- State the empirical and molecular formula for ethane.
- Alkanes are organic compounds with the formula  $C_nH_{2n+2}$ . What is the second smallest value of  $n$  for which the empirical formula is different from the molecular formula?

##### Part A

Substituting  $n = 2$  in  $C_nH_{2n+2}$  gives us the molecular formula:

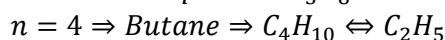
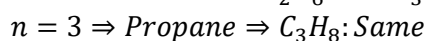
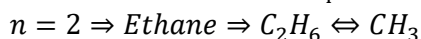
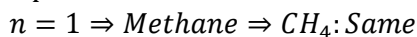


And simplifying gives us the empirical formula:



##### Part B

Start by comparing the molecular and empirical formulas for the alkanes, starting with the smallest value of  $n$ :



*Second smallest value of  $n = 4$*

#### 1.98: Multiple

The empirical formula and molecular formula are connected by the whole number multiple given by

$$\frac{\text{Molar Mass}}{\text{Empirical Mass}}$$

### (Calc) Example 1.99

A compound consists of 40% carbon, 6.71% hydrogen, and 53.29% oxygen. Name the compound, if the molar mass is:

- A.  $180.15 \frac{g}{mole}$
- B.  $90.08 \frac{g}{mole}$

Suppose we have 100 g of the compound. Then

$$C = \frac{40 g}{12.011 \frac{g}{moles}} = 3.33 \text{ moles}$$

$$H = \frac{6.71 g}{1.008 \frac{g}{moles}} = 6.66 \text{ moles}$$

$$O = \frac{53.29 g}{15.999 \frac{g}{moles}} = 3.33 \text{ moles}$$

$$C_{3.33}H_{6.66}O_{3.33} = C_{\frac{3.33}{6.66}}H_{\frac{6.66}{6.66}}O_{\frac{3.33}{6.66}} = C_{0.5}H_1O_{0.5} = CH_2O$$

The empirical mass is

$$12.011 + 2(1.008) + 15.999 = 30.026$$

Part A

$$\text{Multiple} = \frac{180.15}{30.026} = 6$$

$$C_6H_{12}O_6 \Rightarrow \text{Glucose}$$

Part B

$$\text{Multiple} = 3$$

$$C_3H_6O_3 \Rightarrow \text{Lactic Acid}$$

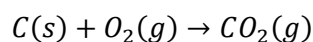
## E. Chemical Equations

### Example 1.100: Extracting Iron from Iron Ore

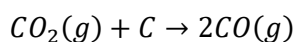
Given the process below which describes the extraction of iron from iron ore, write balanced equations for each step of the process:

1. Coke (*coal*) in the furnace burns (with oxygen) to give carbon dioxide gas.
2. Carbon dioxide reacts with more coke to form carbon monoxide gas.
3. Ferric oxide reacts with carbon monoxide gas to form molten iron and carbon dioxide gas.

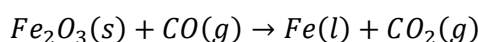
Step 1



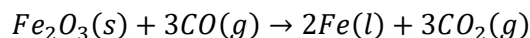
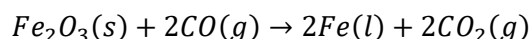
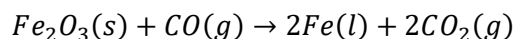
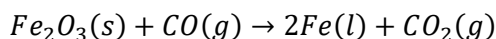
Step 2



Step 3



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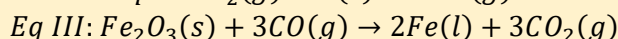
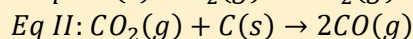
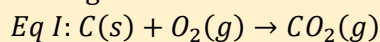


### 1.101: Overall Equation

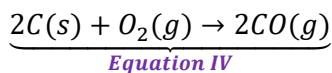
The chemical equations in a reaction can be added to determine the net (*overall*) reaction

### Example 1.102

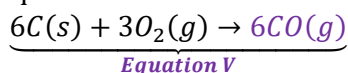
Determine the overall equation for the following set of reactions:



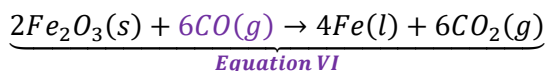
Add Eq I and II:



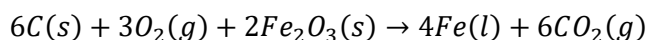
CO is a product in Eq II, and a reactant in Eq III. To make the coefficients equal, multiply Eq IV by 3:



Multiply Eq III by 2



Add Equation V to Equation VI:

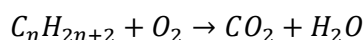


## F. Molar Ratios

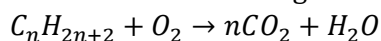
### Example 1.103

5L of an alkane requires 25L of oxygen for its complete combustion. If all volumes are measured at constant temperature and pressure, the alkane is: (JEE Main April 9, 2016)

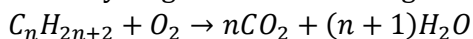
Whenever a compound of carbon and hydrogen burns in excess of air, the products are carbon dioxide and water.



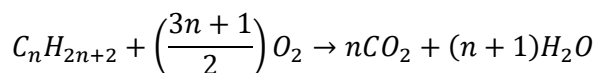
Carbon atoms on the left must match the carbon atoms on the right:



Hydrogen atoms on the left must match the hydrogen atoms on the right:



Oxygen atoms on the right  $2n + n + 1 = 3n + 1$  must match the oxygen atoms on the left:



5L Alkane: 25 L Oxygen

Simplify and convert to moles since  $\text{moles} \propto \text{volume}$ :

$$\underbrace{1 \text{ mol Alkane}}_A : \underbrace{5 \text{ mol Oxygen}}_O$$

If I multiply the number of moles of the Alkane by 5, I will get the number of moles of oxygen:

$$5A = O$$

Substitute  $A = 1, O = \frac{3n+1}{2}$ :

$$1(5) = \frac{3n+1}{2} \Rightarrow 10 = 3n+1 \Rightarrow n = 3 \Rightarrow \text{Propane}$$

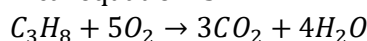
## G. Limiting Reactant

### 1.104: Limiting reactant

#### Example 1.105

100 g of propane burns in 100 g of oxygen. Determine the mass of carbon dioxide, and mass of water produced.

The balanced chemical equation is:



	Mass(g)	Molar mass	Moles
$C_3H_8$	100	44.097	2.26
$O_2$	100	32	3.125

The ratio of propane to oxygen is:

$$1:5$$

Multiply both sides of the above by 2.26:

$$1:5 = \underbrace{2.26}_{C_3H_8} : \underbrace{11.3}_{O_2}$$

Hence, oxygen is the limiting reagent. The number of moles of carbon dioxide produced based on the complete combustion of given moles of oxygen is:

$$3.125 \times \frac{3}{5} = 1.875 \text{ mol of } CO_2$$

Mass of carbon dioxide

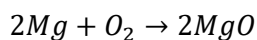
$$= (1.875)(44) = 82.5 \text{ g}$$

Mass of water

$$= (3.125)\left(\frac{4}{5}\right)(18) = 45 \text{ g}$$

#### Example 1.106

1.0 g of magnesium is burnt with 0.56 g  $O_2$  in a closed vessel. Which reactant is left in excess and how much?  
 (NEET 2014)



$$\text{Moles of magnesium} = \frac{1}{24}$$

$$\text{Moles of Oxygen} = \frac{0.56}{32} = \frac{56}{3200} = \frac{7}{400}$$

Excess magnesium (if any) will be

$$= 24\left(\frac{1}{24} - 2 \cdot \frac{7}{400}\right) = 1 - 12 \cdot \frac{7}{400} = 1 - \frac{84}{100} = 0.16 \text{ g}$$

## H. Yields

### 1.107: Percentage Yield

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}}$$

Where:

- Theoretical yield is the yield from the chemical equation for a reaction.
- Actual yield is the yield from running a chemical reaction in a laboratory or a factory.

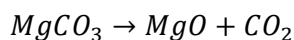
### Example 1.108

100 g of propane burns in 100 g of oxygen. In the example above, we calculated yield of carbon dioxide as 82.5 g, and yield of water as 45 g. Is this actual, theoretical, or percentage yield?

*Theoretical*

### Example 1.109

20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample? (At. Wt. of Mg= 24) (NEET 2015)



Molar mass of  $\text{MgCO}_3$

$$= 24 + 12 + 3(16) = 84 \text{ g}$$

Molar mass of  $\text{MgO}$

$$= 24 + 16 = 40 \text{ g}$$

Theoretical yield of magnesium carbonate from the equation

$$= \frac{40}{84}$$

Theoretical yield of magnesium carbonate for 20 g

$$= 20 \times \frac{40}{84} \approx 9.52 \text{ g}$$

Actual yield

$$= 8 \text{ g}$$

$$\% \text{ purity} = \% \text{ yield} = \frac{8}{9.52} = 84\%$$



## 2. GASES

### 2.1 Pressure

#### A. Pressure

##### 2.1: Proportionality

$$A \propto B \Leftrightarrow A = kB$$

Where

$$k = \text{Some constant}$$

##### 2.2: Pressure

Pressure is force perpendicular to the surface of an object per unit area over which that force is distributed.

$$P = \frac{F}{A}$$

##### Example 2.3

*Mark all correct options*

Considering other variables constant, pressure on the surface of an object is

- A. directly proportional to force
- B. inversely proportional to force
- C. directly proportional to area
- D. inversely proportional to area

From  $P = \frac{F}{A}$ , we get:

$$P \propto F \Rightarrow \text{Option A}$$

$$P \propto \frac{1}{A} \Rightarrow \text{Option D}$$

*Options A, D*

##### Example 2.4

*Mark the correct option*

Which of the following statements is wrong for gases?

- A. Confined gas exerts uniform pressure on the walls of its container in all directions.
- B. Volume of the gas is equal to volume of container confining the gas.
- C. Gases do not have a definite shape and volume.
- D. Mass of a gas cannot be determined by weighing the container in which it is enclosed. (NEET 1999)

Mass of gas

$$= \text{Mass of cylinder with Gas} - \text{Mass of Cylinder without gas}$$

Option D is wrong.

*Option D*

##### 2.5: SI Units of Pressure

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

$$1 \text{ kPa} = 1000 \text{ Pa}$$

$$1 \underbrace{N}_{\text{Force}} = \underbrace{kg}_{\text{mass}} \cdot \underbrace{\frac{m}{s^2}}_{\text{acceleration}}$$

## B. Measuring Air Pressure

### 2.6: Pressure at sea level

The pressure of the atmosphere at sea level at  $0^\circ\text{C}$

$$= 1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa} = 1.01325 \text{ Bar}$$

Where

$$\begin{aligned} \text{atm} &= \text{atmosphere} \\ \text{mmHg} &= \text{millimeters of mercury} \\ \text{torr} &= \text{mmHg} \end{aligned}$$

### Example 2.7

Convert 1 mmHg to atm.

$$\frac{1}{760} \text{ atm}$$

### 2.8: Barometer

A barometer is a device to measure air pressure. It consists of a mercury filled tube immersed in a vessel of mercury.

- Pressure is measured as the height  $h$  of the column above the liquid.
- Mercury is used since it is a very dense liquid, reducing the height of the tube.

### Example 2.9

You measure the air pressure in a  $5\text{m} \times 5\text{m} \times 5\text{m}$  open room at sea level at  $0^\circ\text{C}$ , and then the air pressure in a  $100\text{m} \times 100\text{m} \times 20\text{m}$  stadium at sea level at  $0^\circ\text{C}$ . The pressure in the stadium, as compared to the room:

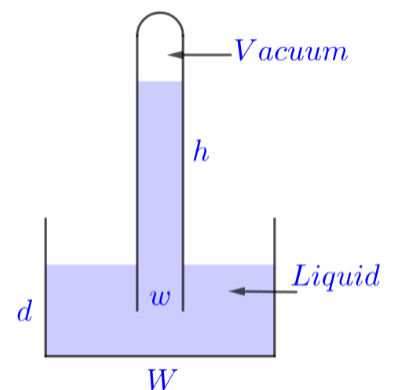
- A. Will be more
- B. Will be less
- C. Cannot be determined
- D. None of the above

### Example 2.10

Answer each part separately

The barometer drawn alongside has width of vessel  $W$ , depth of liquid  $d$  in the vessel, width of tube  $w$ , and height of column  $h$  above the surface of the liquid. Explain the effect on the barometer reading of:

- A. Increase in  $W$
- B. Decrease in  $w$
- C. Increase in  $d$
- D. Increase in  $h$



For options A, B, and C, there is no change.

For Option A:

There is an increase in  $W$ . The downward force due to air increases. Correspondingly, the area also increases.  
 There is no net change.

*Reading Increases  $\Rightarrow$  Increase in air pressure*

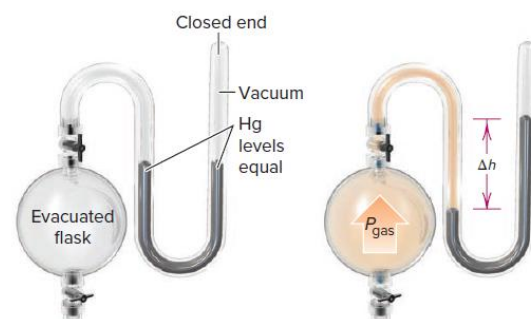
### 2.11: Closed ended Manometer

A manometer is a device used to measure the pressure of gas in an experiment. In a closed-ended manometer:

$$\text{Pressure of gas} = P_{\text{gas}} = \Delta h$$

Where

$h$  is measured in mmHg



#### Example 2.12

In the adjoining diagram,  $\Delta h = 200 \text{ mmHg}$ . Find the pressure of the gas.

$$\text{Pressure} = 200 \text{ mmHg}$$

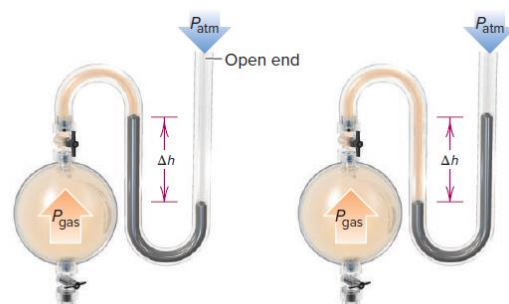
### 2.13: Open ended Manometer

If left mercury level is higher, then the pressure of the gas is less than atmospheric pressure and:

$$P_{\text{gas}} = P_{\text{atm}} - \Delta h$$

If right mercury level is higher, then the pressure of the gas is higher than atmospheric pressure and:

$$P_{\text{gas}} = P_{\text{atm}} + \Delta h$$



#### Example 2.14

In the adjoining diagram,  $\Delta h = 200 \text{ mmHg}$ . Find the pressure of the gas.

$$\text{Left Diagram: Pressure} = 760 - 200 = 560 \text{ mmHg}$$

$$\text{Right Diagram: Pressure} = 760 + 200 = 960 \text{ mmHg}$$

## 2.2 Ideal Gases

### A. Ideal Gas Law

#### 2.15: Ideal Gas Law

$$PV = nRT$$

Where

$P$  = Pressure

$V$  = Volume

$n$  = number of moles = Amount of gas

$R$  = gas constant

$T$  is measured in Kelvin

- Ideal gases do not exist in reality.
- Ideal gas law is an approximation for the behavior of real gases.

$$R = \frac{PV}{nT} \Rightarrow R \text{ has units } \frac{\text{Pressure} \cdot \text{Volume}}{\text{Amount} \cdot \text{Temperature}}$$

## 2.16: Relation between $K$ and $C$

$$K = C + 273.15$$

### Example 2.17

The volume occupied by 1.8 gram of water vapor at  $374^\circ\text{C}$  and 1 bar pressure will be [Use  $R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$ ] (answer in Liters, to one significant figure) (NEET 2019, Adapted)

$$PV = nRT \Rightarrow V = \frac{nRT}{P}$$

Substitute  $P = 1, n = \frac{m}{M} = \frac{1.8}{18} = 0.1, K = 273 + 374 \approx 650$ :

$$= \frac{(0.1)(0.083)(650)}{1} \approx \frac{80 \times 650}{10,000} = \frac{520}{100} = 5.2 \approx 5$$

### Example 2.18

Mark the correct option

In the gas equation,  $PV = nRT$ :

- $n$  is the number of molecules of a gas
- $V$  denotes volume of one mole of the gas
- $n$  moles of the gas have a volume  $V$
- $P$  is the pressure of the gas when only one mole of gas is present. (NEET 1992)

$n = \text{no. of moles} \Rightarrow \text{Option A is incorrect}$

$V = \text{Volume of } n \text{ moles of gas} \Rightarrow \text{Option B is incorrect}$

$P = \text{pressure due to } n \text{ moles} \Rightarrow \text{Option D is incorrect}$

Option C is correct

### Example 2.19

Correct gas equation is:

- $\frac{V_1 T_2}{P_1} = \frac{V_2 T_1}{P_2}$
- $\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$
- $\frac{P_1 T_1}{V_1} = \frac{P_2 V_2}{T_2}$
- $\frac{V_1 V_2}{T_1 T_2} = P_1 P_2$  (NEET 1989)

The options only have  $V, T$  and  $P$  so we want the relation between volume, temperature and pressure without taking  $n$  or  $R$  into account.,

Rearrange the ideal gas equation to get:

$$PV = nRT \Rightarrow nR = \frac{PV}{T} = \text{Constant}$$

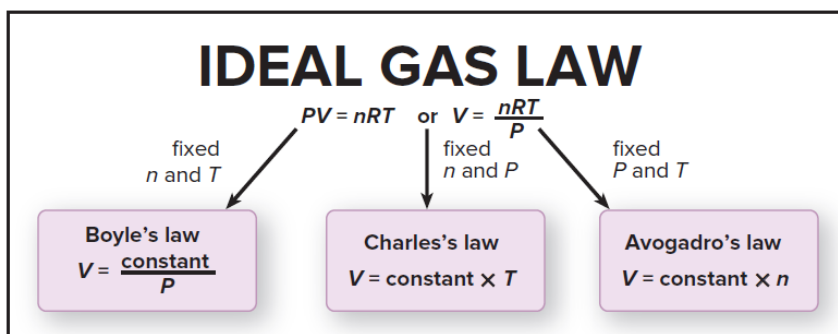
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Rearrange:

$$\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$$

*Option B is correct*

## 2.20: Special Cases



## B. Boyle's Law

### 2.21: Boyle's Law

If temperature is fixed, the pressure of an amount of gas is inversely proportional to volume.

$$P \propto \frac{1}{V} \Leftrightarrow PV = \text{Constant}$$

### Example 2.22

*True or False*

In the ideal gas law, if  $n$  and  $T$  are fixed, then  $PV = R$

$$PV = nRT \neq R$$

*False*

### Example 2.23

The initial volume of a gas cylinder is 750.0 mL. If the pressure of gas inside the cylinder changes from 840.0 mmHg to 360.0 mmHg, the final volume of the gas will be: (JEE Main, April 11, 2014)

Since  $T$  and  $n$  are constant:

$$PV = \text{Constant} \Rightarrow P_1 V_1 = P_2 V_2$$

Rearranging, and substituting values from the question:

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{(840)(750)}{360} = 1750 \text{ mL}$$

### Example 2.24

A spherical balloon of radius 3 cm containing helium gas has a pressure of  $48 \times 10^{-3}$  bar. At the same temperature, the pressure, of a spherical balloon of radius 12 cm containing the same amount of gas will be  $\text{---} \times 10^{-6}$  bar. (JEE Main, Sep 6, 2020, Shift-I)

Using similarity of spheres, the ratio of volumes is the cube of the ratio of radii:

$$\frac{V_2}{V_1} = \left(\frac{r_2}{r_1}\right)^3 = \left(\frac{3}{12}\right)^3 = \left(\frac{1}{4}\right)^3 = \frac{1}{64}$$

Since  $T$  and  $n$  are constant:

$$PV = \text{Constant}$$

Rearranging  $P_1 V_1 = P_2 V_2$ , and substituting  $P_2 = 48 \times 10^{-3}$ ,  $\frac{V_2}{V_1} = \frac{1}{64}$ :

$$P_1 = P_2 \frac{V_2}{V_1} = (48 \times 10^{-3}) \left(\frac{1}{64}\right) = 0.75 \times 10^{-3} = 750 \times 10^{-6}$$

### Example 2.25

For 1 mol of an ideal gas at a constant temperature, the plot of  $(\log P)$  against  $(\log V)$  is a (P: Pressure, V: Volume):

- A. Straight line parallel to  $x$ -axis
- B. Straight line with a negative slope
- C. Curve starting at origin
- D. Straight line passing through origin. (JEE Main, May 7, 2012)

Since  $T$  and  $n$  are constant:

$$PV = K, K = \text{Constant}$$

Take the log both sides:

$$\log(PV) = \log K$$

Use  $\log ab = \log a + \log b$

$$\log P + \log V = \log K$$

Solve for  $\log P$ :

$$\log P = \log K - \log V$$

We know that  $\log P = y$ ,  $\log V = x$ ,  $\log K = \text{Constant}$ :

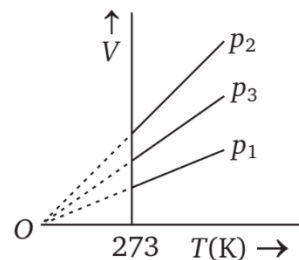
$$y = \text{Constant} - x$$

Which is a straight line with slope  $-1$ .

Option B

### Example 2.26

The volume-temperature graphs of a given mass of an ideal gas at constant pressures are shown below. What is the correct order of pressures in descending order? (EAMCET 2006)



$$PV = nRT$$

$n$  is constant. When we compare the graphs vertically, temperature is also constant. Hence:

$$PV = \text{Constant}$$

Hence, increase in volume leads to decrease in pressure. Volumes are in the sequence:

$$p_2 > p_3 > p_1$$

Pressures will be in the reverse sequence

$$p_1 > p_3 > p_2$$

## C. Avogadro's and Charles' Law

### 2.27: Avogadro's Law

If temperature and pressure are constant, the volume of a gas is proportional to its amount.

$$V \propto n \Leftrightarrow V = n \cdot \text{Constant}$$

Where:

$$n = \text{number of moles} = \text{Amount of gas}$$

### 2.28: Charles' Law

If the pressure is constant, the volume of a fixed amount of gas is proportional to its temperature.

$$V \propto T$$

$$V = T \cdot \text{constant}$$

Where

$$T \text{ is measured in Kelvin}$$

### Example 2.29

Which of the following is a representation of Charles' law?

- A.  $p_1 T_1 = p_2 T_2$
- B.  $p_1 T_2 = p_2 T_1$
- C.  $p_1 V_1 = p_2 V_2$
- D.  $V_1 T_2 = V_2 T_1$  (EAMCET 1995)

$$V = KT \Rightarrow \frac{V}{T} = K$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow V_1 T_2 = V_2 T_1 \Rightarrow \text{Option D}$$

### Example 2.30

True or False

Charles' Law holds when  $T$  is measured in degrees Celsius.

$$V \propto T$$

$$V = TK, K = \text{Constant}$$

Substitute  $T = C + 273$ :

$$V = (273 + C)K$$

$$V = 273K + CK$$

Because of the constant factor  $273K$ :

$$V \text{ is not } \propto CK$$

### Example 2.31

An open vessel at  $27^\circ\text{C}$  is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is: (JEE Main May 19, 2012; JEE Main Jan 12, 2019, Shift-II)

Pressure is atmospheric pressure and remains constant.

Volume of the vessel is constant.

Pressure and volume are constant in  $PV = nRT$

$$1 = nT \times \text{Constant} \Rightarrow nT = \frac{1}{\text{Constant}}$$

$$\begin{aligned} n_1 T_1 &= n_2 T_2 \\ n(273 + 27) &= \left(\frac{3}{5}n\right) T_2 \\ T_2 &= 500K \end{aligned}$$

### Example 2.32

A bubble of air is underwater at temperature  $15^\circ\text{C}$  and the pressure 1.5 bar. If the bubble rises to the surface where the temperature is  $25^\circ\text{C}$  and the pressure is 1.0 bar, what will happen to the volume of the bubble?

- A. Volume will become greater by a factor of 1.6.
- B. Volume will become greater by a factor of 1.1.
- C. Volume will become smaller by a factor of 0.70.
- D. Volume will become greater by a factor of 2.5. (NEET 2011)

$$PV = nRT$$

$n$  = amount of air in bubble is constant, and  $R$  is a constant:

$$\frac{PV}{T} = \text{Constant}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

We want to compare new volume with old volume, which means we need ratio of volumes:

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{T_1 P_2} = \frac{(1.5)(298)}{(288)(1)} \approx 1.6$$

Option A

## D. Concentration

### 2.33: Standard Temperature and Pressure (STP)

STP means

$$\text{Temperature} = 0^\circ\text{C} = 273.15K$$



$$Pressure = 1 \text{ atm} = 760 \text{ mmHg}$$

At STP, helium, nitrogen, oxygen and other simple gases behave nearly ideally.

### 2.34: Standard molar volume

The volume of 1 mol of an ideal gas at STP is

$$\text{Standard molar volume} = 22.4141 \text{ L} \approx 22.4 \text{ L}$$

### 2.35: Value of R

$$R = 0.082057 \approx 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}}$$

Where

$\text{atm} = \text{pressure}$

$\text{L} = \text{volume}$

$\text{mol} = n$

$\text{K} = \text{temperature}$

Consider an ideal gas at STP.

$$PV = nRT \Rightarrow R = \frac{PV}{nT}$$

Substitute  $P = 1 \text{ atm}$ ,  $V = 22.4 \text{ L}$ ,  $n = 1 \text{ mol}$ ,  $T = 273.15 \text{ K}$

$$= \frac{1 \text{ atm} \cdot 22.4 \text{ L}}{1 \text{ mol} \cdot 273.15 \text{ K}} = 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}}$$

### Example 2.36

The correct value of the gas constant  $R$  is close to

- A. 0.082 litre-atmosphere K
- B. 0.082 litre-atmosphere  $\text{K}^{-1} \text{ mol}^{-1}$
- C. 0.082 litre-atmosphere $^{-1} \text{ K mol}^{-1}$
- D. 0.082 litre $^{-1}$  atmosphere $^{-1} \text{ K mol}$  (NEET 1992)

Option B

### 2.37: Concentration

Concentration of a gas is measured in moles of gas per liter of volume

$$= \frac{\text{Quantity}}{\text{Volume}} = \frac{\text{mol}}{\text{L}}$$

### Example 2.38

Under what conditions, if any, will a pure sample of an ideal gas not only exhibit a pressure of 1 atm but also a concentration of 1 mol liter $^{-1}$ . Use  $R = 0.082 \text{ liter atm mol}^{-1} \text{ deg}^{(-1)}$  and answer to two significant digits). (NEET 1993, Adapted)

$$PV = nRT$$

Substitute  $P = 1 \text{ atm}$ ,  $R = 0.082$ , Concentration = 1  $\frac{\text{mol}}{\text{litre}} \Rightarrow n = 1, V = 1$ :

$$(1)(1) = (1)(0.082)(T)$$

$$T = \frac{1}{0.082} \approx 12K$$

### Example 2.39

$n$  moles of an ideal gas at temperature,  $T$  (in kelvin) occupy  $V$  L of volume, exerting a pressure of  $p$  atmospheres. What is the concentration (in  $\frac{\text{mol}}{\text{L}}$ )? (EAMCET 2001)

Rearrange  $pV = nRT$ :

$$\frac{\text{mol}}{\text{L}} = \frac{n}{V} = \frac{p}{RT}$$

## E. Molar Mass

### 2.40: Value of R (Alternate)

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}$$

Convert  $1 \text{ atm} \cdot \text{L} = 101,325 \text{ Pa} \times 1,000 \text{ cm}^3$  to meters:

$$101,325 \text{ Pa} \times 1,000 \times \frac{1}{1,000,000} \text{ m}^3$$

Simplify:

$$= 101.325 \text{ Pa} \cdot \text{m}^3$$

Substitute  $J = \text{Pa} \cdot \text{m}^3$ :

$$= 101.325 \text{ J}$$

$$R = 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} = 0.0821 \frac{101.325 \text{ J}}{\text{mol} \cdot \text{K}} \approx 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

### 2.41: Ideal Gas Equation (Molar Mass Version)

$$PV = \frac{m}{\mathcal{M}} RT \Leftrightarrow \mathcal{M} = \frac{mRT}{PV}$$

Where

$m = \text{mass in g}$

$\mathcal{M} = \text{molar mass:}$

$$PV = nRT$$

Substitute  $n = \frac{m}{\mathcal{M}}$  where  $m = \text{mass in g}$ ,  $\mathcal{M} = \text{molar mass}$ :

$$PV = \frac{m}{\mathcal{M}} RT$$

Solve for  $\mathcal{M}$ :

$$\mathcal{M} = \frac{mRT}{PV}$$

### Example 2.42

The pressure exerted by 6.0 g of methane gas in a 0.03 m<sup>3</sup> vessel at 129°C is (Atomic masses: C = 12.01, H = 1.01 and R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>)

- A. 215,216 Pa
- B. 13,409 Pa
- C. 41,648 Pa
- D. 31,684 Pa (NEET 2010)

$$PV = \frac{m}{\mathcal{M}}RT$$

Substitute  $V = 0.03\text{m}^3$ ,  $m = 6\text{g}$ ,  $\mathcal{M}(\text{CH}_4) = 12.01 + 4(1.01) = 16.05$

$$P(0.03) = \frac{6}{16.05}(8.314)(402)$$

$$P = \frac{6(8.314)(402)}{16.05(0.03)}$$

Multiply numerator and denominator by 1000 to remove decimal point:

$$P = \frac{6(8314)(402)(10)}{(1605)(3)}$$

Approximate  $\frac{402}{1605} \approx \frac{1}{4}$

$$P = \frac{6(8314)(10)}{4(3)}$$

$$P = \frac{83140}{2} \Rightarrow \text{Option C}$$

## 2.3 Ideal Gas Law: Rearrangements

### A. Density

#### 2.43: Density

$$\text{Density} = d = \rho = \frac{\text{Mass}}{\text{Volume}} = \frac{m}{V} = \frac{g}{L}$$

Where

$$m = \text{mass}$$

$$V = \text{volume}$$

#### Example 2.44

Calculate the density of oxygen at STP (to three significant figures).

Consider 1 mol oxygen at STP.

It will have\

$$m = 32\text{g}, V = 22.4\text{ L}$$

$$d = \frac{m}{V} = \frac{32\text{ g}}{22.4\text{ L}}$$

Removing decimals and simplifying:

$$= \frac{320}{224} = \frac{10}{7}$$

Approximating using long division:

$$\approx 1.43 \frac{g}{L}$$

### Example 2.45

If  $P$ ,  $V$ ,  $M$ ,  $T$  and  $R$  are pressure, volume, molar mass, temperature and gas constant respectively, then for an ideal gas, the density is given by

- A.  $\frac{RT}{PM}$
- B.  $\frac{P}{RT}$
- C.  $\frac{M}{V}$
- D.  $\frac{PM}{RT}$  (NEET 1989)

Substitute  $n = \frac{m}{M}$  in  $PV = nRT$

$$PV = \frac{m}{M}RT$$

$$\rho = \frac{m}{V} = \frac{PM}{RT}$$

Option D

### 2.46: Ideal Gas Law (Density Version)

$$\rho = \frac{PM}{RT}$$

### Example 2.47

Mark all correct options

Recall that the proportionality symbol  $\propto$  indicates that a change in one side results in a change in the other side. In an ideal gas, other variables being held constant:

- A.  $\rho \propto P$
- B.  $\rho \propto M$
- C.  $\rho \propto \frac{1}{R}$
- D.  $\rho \propto \frac{1}{T}$

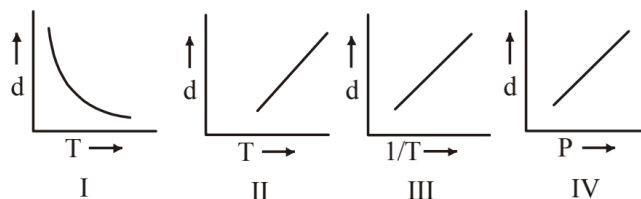
Options A, B and D are correct.

$$\rho \propto R \Rightarrow \rho = KR$$

But  $R$  does not change with change in density. So Option C is not correct.

### Example 2.48

If  $d = \text{density}$ ,  $P = \text{Pressure}$ ,  $T = \text{Temperature}$ , which one of the graphs is not correct for ideal gas? (JEE Main Sep 2, 2020, Shift-I)



$$\rho = \frac{PM}{RT}$$

We must assume that other quantities are constant except the graphed ones.

$$\rho \propto P \Rightarrow d \text{ vs } P \text{ is a line} \Rightarrow \text{Graph IV is correct}$$

$$\rho T \propto 1$$

$\rho$  vs  $\frac{1}{T}$  is a line with positive slope  $\Rightarrow$  III is correct

$\rho$  vs  $T$  is a Rectangular Hyperbola  $\Rightarrow$  I is correct, II is wrong

### Example 2.49

What is the density of  $N_2$  gas at  $227^\circ\text{C}$  and 5.00 atm pressure? ( $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ) (Answer to one significant figure) (NEET 2013)

$$\rho = \frac{PM}{RT} = \frac{(5)(28)}{(0.082)(500)} = \frac{28}{8.2} = \frac{14}{4.1} = \frac{140}{41} \approx 3 \frac{\text{g}}{\text{L}}$$

### Example 2.50

Assuming ideal gas behavior, the ratio of density of ammonia to that of hydrogen chloride at same temperature and pressure is: (Atomic wt. of Cl = 35.5u)

- A. 1.46
- B. 1.64
- C. 0.46
- D. 0.64 (JEE Main April 16, 2018)

$$\rho = \frac{PM}{RT}$$

Here, temperature and pressure are constant, so  $\rho \propto M$

$$\rho_{NH_3} : \rho_{HCl} = 17 : 36.5 < \frac{1}{2} \Rightarrow \text{Option C}$$

### Example 2.51

At 300 K, the density of a certain gaseous molecule at 2 bar is double to that of dinitrogen ( $N_2$ ) at 4 bar. The molar mass of gaseous molecule is: (JEE Main April 9, 2017)

The density of the gaseous molecule is twice the density of  $N_2$ :

$$\rho = 2\rho_{N_2}$$

Use  $\rho = \frac{PM}{RT}$ :

$$\frac{2M}{RT} = 2 \left( \frac{4 \times 28}{RT} \right)$$

$$M = 4 \times 28 = 112$$

Logical Method

$$\text{Molar Mass} = \underbrace{2}_{\text{Density Factor}} \times \underbrace{2}_{\text{Pressure Factor}} \times 28 = 112$$

## 2.52: Ratio of densities

## B. Partial Pressures

### 2.53: Dalton's Law of Partial Pressures

In a mixture of *unreacting gases*, the total pressure is the sum of the partial pressures of the individual gases.

$$P_{Total} = P_1 + P_2 + P_3 + \dots$$

$$\text{Pressure from Gas}_1 = P_1 = \frac{n_1 RT}{V}$$

$$\text{Pressure from Gas}_2 = P_2 = \frac{n_2 RT}{V}$$

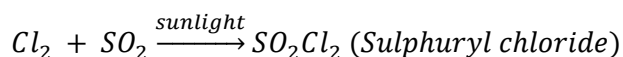
$$\text{Pressure from Gas}_3 = P_3 = \frac{n_3 RT}{V}$$

### Example 2.54

Which of the following mixtures of gases does not obey Dalton's law of partial pressure?

- A.  $Cl_2$  and  $SO_2$
- B.  $CO_2$  and  $He$
- C.  $O_2$  and  $CO_2$
- D.  $N_2$  and  $O_2$  (NEET 1996)

Options B, C and D are combinations are found in the atmosphere and do not react.



### Example 2.55

0.5 moles of gas A and  $x$  moles of gas B exert a pressure of 200 Pa in a container of volume  $10 \text{ m}^3$  at 1000K. Given  $R$  is the gas constant in  $JK^{-1} \text{ mol}^{-1}$ ,  $x$  is: (Answer in terms of  $R$ ) (JEE Main, Jan 9, 2019, Shift-I)

$$PV = nRT$$

Substitute  $P = 200 \text{ Pa}$ ,  $V = 10 \text{ m}^3$ ,  $n = 0.5 + x$ ,  $T = 1000$ :

$$(200)(10) = (0.5 + x)R(1000)$$

$$2 = 0.5R + xR$$

$$x = \frac{2 - 0.5R}{R} = \frac{4 - R}{2R}$$

### 2.56: Partial Pressure Formula

The pressure due to gas A in a mixture of gases is the total pressure multiplied by the mole fraction of A.

$$P_A = X_A \times P_{Total}$$
$$P_A \propto X_A$$

Where

$X_A$  is the mole fraction, given by

$$\frac{\text{Moles of A}}{\text{Total Moles in the mixture}}$$

### Example 2.57

A gaseous mixture was prepared by taking equal moles of  $CO$  and  $N_2$ . If the total pressure of the mixture was found to be 1 atmosphere, the partial pressure of the nitrogen ( $N_2$ ) in the mixture is: (NEET 2011)

$$n(CO) = n(N_2)$$

$$P_{CO} = P_{N_2} = \frac{1}{2} \text{ atm}$$

### Example 2.58

A mixture of  $N_2$  and  $Ar$  gases in a cylinder contains 7 g of  $N_2$  and 8 g of  $Ar$ . If the total pressure of the mixture of the gases in the cylinder is 27 bar, the partial pressure of  $N_2$  is [Use atomic masses (in  $g \text{ mol}^{-1}$ ):  $N = 14, Ar = 40$ ] (NEET 2020)

$$\text{Moles of } N_2 = \frac{7}{28} = \frac{1}{4} = 0.25$$

$$\text{Moles of } Ar = \frac{8}{40} = \frac{1}{5} = 0.2$$

The mole fraction of  $N_2$

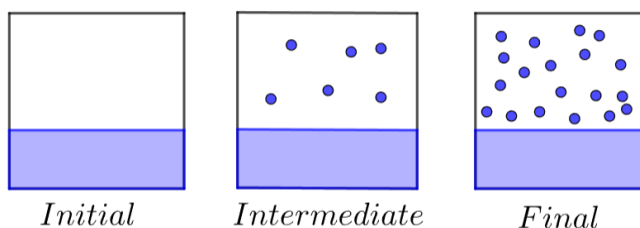
$$= \frac{\text{Moles of } N_2}{\text{Total Moles}} = \frac{0.25}{0.25 + 0.2} = \frac{0.25}{0.45} = \frac{25}{45} = \frac{5}{9}$$

The partial pressure due to nitrogen is:

$$= X_{N_2} \times P_{\text{Total}} = \frac{5}{9} \times 27 = 15 \text{ bar}$$

### C. Vapor Pressure

- Imagine a closed container partly filled with water, and the rest is air. (*Initial Diagram*).
- At the border of the water, some water molecules will escape and become water vapor. (*Intermediate Diagram*)
- Eventually, equilibrium will be established when the number of molecules escaping the water are the same as the number of molecules converting back into water. (*Final Diagram*)



### 2.59: Vapor Pressure

When a solid or liquid comes in contact with a gas, some particles escape into the gas, creating vapor. Eventually, equilibrium is established. The pressure at equilibrium is vapor pressure.

- Vapor pressure depends only on the temperature.

### Example 2.60

If  $10^{-4} \text{ dm}^3$  of water is introduced into a  $1.0 \text{ dm}^3$  flask at  $300\text{K}$ , how many moles of water are in the vapor phase after equilibrium is established? (Given vapor pressure of  $H_2O$  at  $300\text{K}$  is  $3170 \text{ Pa}$ ,  $R = 8.314 \frac{\text{J}}{\text{K mol}}$ )

- A.  $5.56 \times 10^{-3} \text{ mol}$
- B.  $1.53 \times 10^{-2} \text{ mol}$
- C.  $4.46 \times 10^{-2} \text{ mol}$
- D.  $1.27 \times 10^{-3} \text{ mol}$  (JEE Main 2010)

$10^{-4} \text{ dm}^3$  is miniscule compared to  $1.0 \text{ dm}^3$  and hence we can ignore it.

$$PV = nRT \Rightarrow n = \frac{PV}{RT}$$

Substitute  $P = 3170 \text{ Pa} \approx 3170 \times 10^{-5} \text{ atm}$ ,  $R = 0.0821 \frac{\text{atm L}}{\text{K mol}}$ ,  $T = 300 \text{ K}$ ,  $V = 1.0 \text{ dm}^3 = 1 \text{ L}$

$$n = \frac{(3170 \times 10^{-5})(1)}{(0.0821)(300)}$$

Substitute  $\frac{3170}{300} \approx 10$ ,  $0.0821 \approx \frac{1}{12}$ :

$$= \frac{(10 \times 10^{-5})}{\left(\frac{1}{12}\right)} = 120 \times 10^{-5} = 1.2 \times 10^{-3} \Rightarrow \text{Option D}$$

### Example 2.61

A cylinder containing a mixture of  $\text{CO}$  and  $\text{CO}_2$  has a pressure of  $2.00 \text{ atm}$  at  $93^\circ\text{C}$  ( $366 \text{ K}$ ). The cylinder is then cooled to  $-90^\circ\text{C}$  ( $183 \text{ K}$ ), where  $\text{CO}$  is still a gas but  $\text{CO}_2$  is a solid with a vapor pressure of  $0.25 \text{ atm}$ . The pressure in the cylinder at this temperature is  $0.90 \text{ atm}$ . What is the mole fraction of  $\text{CO}_2$  in the cylinder? (USNCO/Local 2021/17)

Apply Dalton's law of partial pressures at  $183 \text{ K}$ :

$$P_{\text{CO}} + P_{\text{CO}_2} = 0.9$$

$$P_{\text{CO}} = 0.9 - P_{\text{CO}_2} = 0.90 - 0.25 = 0.65$$

Compare the situation at  $366 \text{ K}$  with the situation at  $183 \text{ K}$  for  $\text{CO}$ :

$$P = \frac{nRT}{V}, n \text{ and } V \text{ are constant} \Rightarrow P \propto T$$

$$P_{\text{CO}}(366 \text{ K}) = 0.65 \cdot \frac{T_2}{T_1} = 0.65 \left( \frac{366}{183} \right) = 0.65(2) = 1.3$$

Apply Dalton's law of partial pressures at  $366 \text{ K}$ :

$$P_{\text{CO}} + P_{\text{CO}_2} = 2.0$$

$$P_{\text{CO}_2} = 2 - P_{\text{CO}} = 2 - 1.3 = 0.7$$

$$\text{Mole Fraction}(\propto \text{Partial Pressure}) = \frac{P_{\text{CO}_2}}{\text{Total Pressure}} = \frac{0.7}{2} = 35\%$$

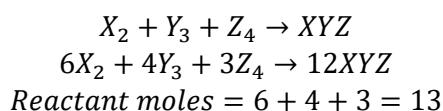
## D. Reaction Stoichiometry

### Example 2.62

An insulated container with a fixed pressure contains ideal gases  $X_2$ ,  $Y_3$  and  $Z_4$ . When the temperature is increased to  $27^\circ\text{C}$ , the gases react to form ideal gas  $XYZ$ . Determine the temperature after the reaction completes.

Note:  $X$ ,  $Y$  and  $Z$  represent unknown chemical elements.

### Determine the balanced equation





$$\text{Product moles} = 12$$

$$\begin{aligned}PV &= nRT \\nT &= \text{Constant} \\n_1T_1 &= n_2T_2 \\(13)(300) &= 12(T_2) \\T_2 &= 325\text{K} = 52^\circ\text{C}\end{aligned}$$

## 2.4 Kinetic Molecular Theory

### A. Kinetic Molecular Theory

A completely quantitative treatment of kinetic molecular theory is college level chemistry. We will *not* derive many of the formulas in this section.

#### 2.63: Kinetic Molecular Theory

Kinetic molecular theory assumes that:

- The volume of a single particle is small enough to be neglected. Particles are equivalent to point masses.
- Particles are in constant, random, straight-line motion, except when collisions happen.
- Collisions are elastic, and frictionless. Hence, their total kinetic energy is constant.
- There are no attractive or repulsive forces between particles.

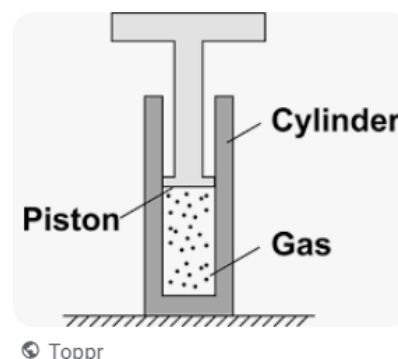
#### 2.64: Pressure

Pressure is caused by particles colliding with container walls.

$$P = \frac{F}{A}$$

#### 2.65: Boyle's Law ( $V \propto \frac{1}{P}$ )

Pushing the piston down leads to decrease in volume. The force from the piston is greater than the force from the gas. A decrease in volume leads to more frequent collisions, and hence an increase in pressure. System is back in equilibrium when the upward pressure balances the downward pressure.



Liquids and solids cannot be compressed because there is very little free space between the particles.

#### 2.66: Law of Partial Pressures ( $P_{\text{Total}} = P_1 + P_2 + \dots$ )

Adding an amount of gas *B* to gas *A* increases the number of particles, which increases the pressure proportionately.

The assumption is that each particle has the same kinetic energy.

#### 2.67: Charles Law ( $V \propto T$ )

Increasing the temperature increases the kinetic energy, which increases the internal pressure. This moves the piston up, until pressures are equal.

$$KE = \frac{1}{2}mv^2, m = \text{mass}, v = \text{velocity}$$

$$T \uparrow \Rightarrow KE \uparrow \Rightarrow v \uparrow \Rightarrow F \uparrow \Rightarrow P \uparrow$$

## 2.68: Avogadro's Law ( $V \propto n$ )

Increasing the amount increases the number of particles, which increases the pressure, moving the piston up until the forces are balanced.

Overall result in an increase in volume.

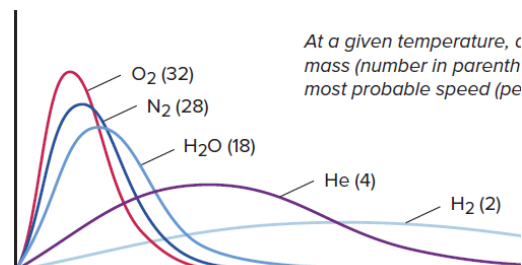
## B. Velocity and Speed

### 2.69: Speed of gas particles

The speed of the gas particles is given by the Maxwell-Boltzmann<sup>1</sup> probability distribution.

For a container at constant temperature, pressure and volume:

- Different particles have different speeds.
- Speed is measured on the  $x$  axis, and the probability corresponding to that speed is measured on the  $y$  axis.
- Lighter gases have a peak to the right of heavier gases. Their overall speed is greater.



### 2.70: Most Likely Speed (Mode)

The most likely velocity is the one that has the highest probability of occurring. It is

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

Where

$v_{mp}$  = most likely speed

### Example 2.71

*Mark all correct options*

A container filled with 1 mole of helium gas at STP is put on a level frictionless surface and does not move. From this, it can be inferred that, for the gas particles, the:

- A. average kinetic energy is zero.
- B. average velocity is zero.
- C. average speed is zero.
- D. temperature is 0K.
- E. pressure is 760 torr.

*Option B*

*Option E*

### 2.72: Average Velocity

The average velocity of a system of particles that form a gas is zero.

<sup>1</sup>The probability distribution of speeds is given by  $f(v) = \left[\frac{m}{2\pi kT}\right]^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2kT}}$  where  $v$  = speed,  $k$  = Boltzmann constant,  $T$  = Temperature,  $m$  = mass of particle.

The individual particles have velocities, but they are in different, random directions, and they overall cancel out.

### 2.73: Average Speed<sup>2</sup> (Mean)

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

### Example 2.74

By what factor does the average speed<sup>3</sup> of a gaseous molecule increase when the temperature (in Kelvin) is doubled? (Answer to three significant figures) (NEET 2011)

$$\begin{aligned}\bar{v} &= \sqrt{\frac{8RT}{\pi M}} \\ \bar{v} &\propto \sqrt{T} \\ \bar{v} &\propto \sqrt{2} = 1.41\end{aligned}$$

## C. Root Mean Square Speed

### 2.75: Root Mean Square (Concept)

$$v = \sqrt{\frac{\sum_{i=1}^n v_i^2}{n}}$$

Consider molecules  $v_1, v_2, \dots, v_n$  with kinetic energy

$$\frac{1}{2}mv_1^2, \frac{1}{2}mv_2^2, \dots, \frac{1}{2}mv_n^2$$

The total kinetic energy of the molecules in an ideal gas is the sum of the kinetic energies of the individual molecules.

$$= \frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \dots + \frac{1}{2}mv_n^2 = \frac{1}{2}m \sum_{i=1}^n v_i^2$$

We can determine the average energy by dividing by the number of molecules:

$$Avg \text{ KE} = \frac{1}{2}m \frac{\sum_{i=1}^n v_i^2}{n} = \frac{1}{2}m \sum_{i=1}^n \frac{v_i^2}{n}$$

Consider a molecule that has “average” kinetic energy:

$$\frac{1}{2}mv^2 = \frac{1}{2}m \sum_{i=1}^n \frac{v_i^2}{n}$$

Cancel  $\frac{1}{2}m$

<sup>2</sup> Average speed can be calculated using  $\int xf(v)$  where  $f(v) = \left[\frac{m}{2\pi kT}\right]^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2kT}}$

<sup>3</sup> The original question says velocity, which is zero.

$$v^2 = \sum_{i=1}^n \frac{v_i^2}{n}$$

$$v = \sqrt{\sum_{i=1}^n \frac{v_i^2}{n}}$$

## 2.76: Root Mean Square Speed (Formula)

$$v_{rms} = \sqrt{\frac{3RT}{\mathcal{M}} \frac{m}{s}}$$

### Example 2.77

For helium gas at standard pressure,  $v_{rms} \propto$  \_\_\_\_\_

R is always constant.

For a specific gas,  $\mathcal{M}$  is also constant. Hence:

$$u_{rms} \propto \sqrt{T}$$

### Example 2.78

The temperature of a gas is raised from  $27^\circ\text{C}$  to  $927^\circ\text{C}$ . The root mean square speed of the gas becomes what factor of its earlier speed: (NEET 1994)

$$v_{rms} \propto \sqrt{T}$$

$$\frac{u_{1-rms}}{u_{2-rms}} = \frac{\sqrt{1200}}{\sqrt{300}} = \sqrt{4} = 2$$

### Example 2.79

Root mean square speed of a gas molecule is proportional to:

- A.  $\mathcal{M}^{\frac{1}{2}}$
- B.  $\mathcal{M}^0$
- C.  $\mathcal{M}^{-\frac{1}{2}}$
- D.  $\mathcal{M}$  (NEET 1990)

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}} \Rightarrow v_{rms} \propto \frac{1}{\sqrt{\mathcal{M}}} = \mathcal{M}^{-\frac{1}{2}} \Rightarrow \text{Option C}$$

## 2.80: Kinetic Energy

From ideal gas law, equimolar samples of any gases exert same pressure and occupy the same volume.

Gases with higher molar mass have lower speed.

## 2.81: Relation between density and speed

$$u_{rms} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

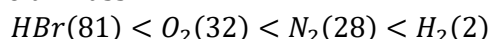
$$v_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}} \Rightarrow v_{rms} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

Ideal gases have the same kinetic energy, independent of their density.  
Hence, gases with higher density must have lower speed, and vice versa.  
This is quantified in the proportionality relation above.

### Example 2.82

Arrange the gases  $H_2$ ,  $N_2$ ,  $O_2$  and  $HBr$  in ascending order based on their root mean square velocity at STP (NEET 1991, Adapted)

We arrange in decreasing order of molar mass:



### 2.83: Relation between temperature and speed

For a specific gas:

$$v_{rms} \propto \sqrt{T}$$

### Example 2.84

If a gas expands at constant temperature, it indicates that:

- A. kinetic energy of molecules remains the same
- B. number of the molecules of gas increases
- C. kinetic energy of molecules decreases
- D. pressure of the gas increases. (NEET 2008)

$n$  remains constant  $\Rightarrow$  Option B is incorrect

$$PV = nRT$$

$V \uparrow \Rightarrow P \downarrow \Rightarrow$  Option D is incorrect

$$v_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}} \Rightarrow v_{rms} \propto \sqrt{T} \Rightarrow \text{Option A}$$

## D. Kinetic Energy

### 2.85: Kinetic Energy

$$\text{Total KE} = \frac{1}{2}mv^2$$

Where

$$v = v_{rms}$$

### 2.86: Kinetic Energy of 1 Mol

$$KE_{\text{Mole}} = \frac{3}{2}RT$$

### Example 2.87

Average molar kinetic energy of  $CO$  and  $N_2$  at same temperature is

- A.  $KE_1 = KE_2$
- B.  $KE_1 > KE_2$
- C.  $KE_1 < KE_2$
- D. can't say anything. Both volumes are not given. (NEET 2000)

Notice how  $KE_1$  and  $KE_2$  are not identified - which refers to which gas. This is because that information is not needed.

$$KE = \frac{3}{2}RT$$

Kinetic energy depends on temperature, not on the nature of the gas.

Option A

### Example 2.88

Mark all correct options

At STP, 0.50 mol  $H_2$  gas and 1.0 mol  $He$  gas

- A. occupy equal volumes
- B. have equal kinetic energy
- C. have equal molecular speeds
- D. have equal number of protons
- E. have equal average kinetic energies

Average kinetic energy means energy per mole, or per molecule.

Option E

### 2.89: Boltzmann Constant

$$\text{Boltzmann constant} = k = \frac{R}{N_A} = 1.380 \times 10^{-23} \frac{J}{K}$$

### 2.90: Kinetic Energy of 1 Molecule

$$KE = \frac{3}{2} \left( \frac{R}{N_A} \right) T = \frac{3}{2} kT$$

$$KE_{Mole} = \frac{3}{2} RT$$

Divide by the number of molecules in one mole (*Avogadro's number*):

$$\frac{KE_{Mole}}{N_A} = \frac{3}{2} \left( \frac{R}{N_A} \right) T$$

Substitute  $\frac{R}{N_A} = k$ :

$$KE_{Molecule} = \frac{3}{2} kT$$

### (Calc) Example 2.91

The average kinetic energy of an ideal gas, per molecule in S.I. units, at 25°C will be (NEET 1996)

$$KE = \frac{3}{2} kT = \left(\frac{3}{2}\right) (1.380 \times 10^{-23})(298) = 6.17 \times 10^{-21} J$$

## E. Comparing Velocities

### Example 2.92

Let  $a$ ,  $b$  and  $c$  be the most probable speed, mean speed and root mean square speed of molecules of an ideal gas. Then find:

- find  $a : b : c$  as an exact ratio (NEET 1993, JEE 2012)
- (Calc) find  $a : b : c$  as a numerical ratio, with  $a = 1$ . (JEE 2013)
- arrange  $a$ ,  $b$  and  $c$  in ascending order (JEE 2012)

Note: Question should read “speed”, but it has been asked in past exam questions with velocity as the keyword.

#### Part A

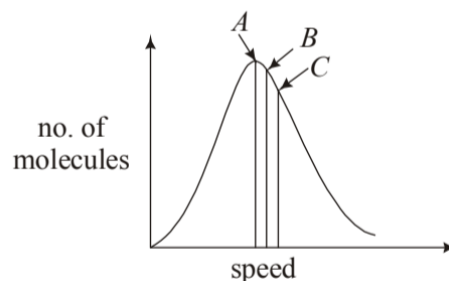
$$v_{mp} : \bar{v} : v_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

#### Part B

$$1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.225$$

#### Part C

$$a < b < c$$



### Example 2.93

Identify the correct labels of  $A$ ,  $B$  and  $C$  in the graph from root mean square speed, most probable speed, and average speed. (JEE Main Jan 07, 2020, Shift-II)

$$\begin{aligned} A &= \text{Most probable} = v_{mp} \\ B &= \text{Average} = \bar{v} \\ C &= \text{RMS} = v_{rms} \end{aligned}$$

### Example 2.94

At 600K, the root mean square ( $rms$ ) speed of gas  $X$  (molar mass = 40) is equal to the most probable speed of gas  $Y$  at 90K. The molar mass of gas  $Y$  is: (JEE Main, April 12, 2023, Shift-I)

$$\begin{aligned} \text{Substitute } T_1 = 600, T_2 = 90, \mathcal{M}_1 = 40 \text{ in } \underbrace{\sqrt{\frac{3RT_1}{\mathcal{M}_1}}}_{v_{rms}} &= \underbrace{\sqrt{\frac{2RT_2}{\mathcal{M}_2}}}_{v_{mp}} \\ \sqrt{\frac{3R \times 600}{40}} &= \sqrt{\frac{2R \times 90}{\mathcal{M}_2}} \\ \sqrt{45R} &= \sqrt{\frac{180R}{\mathcal{M}_2}} \end{aligned}$$

$$45 = \frac{180}{\mathcal{M}_2}$$

$$\mathcal{M}_2 = \frac{180}{45} = 4$$

## F. Graham's Law of Effusion

### 2.95: Graham's Law of Effusion

Effusion is the process by which a gas escapes through a tiny hole in its container into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

### 2.96: Ratio of Effusion of Two Gases

At constant temperature, the ratio of rate of effusion of two gases is:

$$\frac{r_A}{r_B} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

Note that

*LHS and RHS have A and B interchanged in terms of numerator and denominator*

$$\frac{\text{Rate}_A}{\text{Rate}_B} = \frac{\mu_{A-rms}}{\mu_{B-rms}} = \frac{\sqrt{\frac{3RT}{\mathcal{M}_A}}}{\sqrt{\frac{3RT}{\mathcal{M}_B}}} = \frac{\sqrt{\frac{1}{\mathcal{M}_A}}}{\sqrt{\frac{1}{\mathcal{M}_B}}} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

### Example 2.97

Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape? (NEET 2016)

$$\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{\mathcal{M}_{H_2}}{\mathcal{M}_{O_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$$

$$\text{Fraction} = \frac{1}{4} \times \frac{1}{2} = \frac{1}{8}$$

### 2.98: Rate

$$r_A = \frac{V_A}{T_A}$$

Where

$V_A$  = Volume of Gas A  
 $T_A$  = Taken take

Rate is measured in terms of volume of gas that escapes in a given span of time.



### Example 2.99

50 mL of hydrogen diffuses out through a small hole of a vessel, in 20 minutes. The time taken by 40 mL of oxygen to diffuse out is (NEET 1994)

$$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{\mathcal{M}_{O_2}}{\mathcal{M}_{H_2}}}$$

Substitute  $r_{H_2} = \frac{V_{H_2}}{t_{H_2}} = \frac{50 \text{ mL}}{20 \text{ min}} = \frac{5 \text{ mL}}{2 \text{ min}}$ ,  $r_{O_2} = \frac{40}{t}$ :

$$\begin{aligned}\frac{\frac{5}{2}}{\frac{40}{t}} &= \sqrt{\frac{32}{2}} \\ \frac{5}{2} \cdot \frac{t}{40} &= 4 \\ t &= 64 \text{ min}\end{aligned}$$

### 2.100: Time for Effusion

If two gases have the same volume, the ratio of their effusion speeds is the reciprocal of the time taken for effusion:

$$\frac{r_A}{r_B} = \frac{t_B}{t_A} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

$$\frac{r_A}{r_B} = \frac{V/t_A}{V/t_B} = \frac{t_B}{t_A}$$

### Example 2.101

50 mL of each gas A and of gas B takes 150 and 200 seconds respectively for effusing through a pin hole under the similar conditions. If molecular mass of gas B is 36, the molecular mass of gas A will be (NEET 2012)

$$\frac{t_B}{t_A} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

Substitute  $\frac{t_B}{t_A} = \frac{200}{150} = \frac{4}{3}$ ,  $\mathcal{M}_B = 36$

$$\frac{4}{3} = \sqrt{\frac{36}{\mathcal{M}_A}}$$

Square both sides and solve for  $\mathcal{M}_A$ :

$$\mathcal{M}_A = \frac{36 \times 9}{16} = \frac{81}{4} = 20.25$$

### Example 2.102

Two gases A and B having the same volume diffuse through a porous partition in 20 and 10 seconds respectively. The molecular mass of A is 49u. Molecular mass of B will be (NEET 2011)

$$\frac{t_B}{t_A} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

Substitute  $\frac{t_B}{t_A} = \frac{10}{20} = \frac{1}{2}$ :

$$\frac{1}{2} = \sqrt{\frac{\mathcal{M}_B}{49}}$$

Square both sides and solve for  $\mathcal{M}_A$ :

$$\mathcal{M}_B = \frac{49}{4} = 12.25$$

### Example 2.103

At what temperature, the rate of effusion of  $N_2$  would be 1.625 times than the rate of  $SO_2$  at  $50^\circ C$  (NEET 1996)

$$\begin{aligned}\sqrt{\frac{3RT_{N_2}}{\mathcal{M}_{N_2}}} &= 1.625 \sqrt{\frac{3RT_{SO_2}}{\mathcal{M}_{SO_2}}} \\ \sqrt{\frac{T_{N_2}}{28}} &= \frac{13}{8} \sqrt{\frac{323}{64}} \\ T_{N_2} &= \frac{169}{64} \times \frac{323}{64} \times 28\end{aligned}$$

## 2.5 Real Gases

### A. van der Waal's Equation

#### Example 2.104

Mark all correct options

The number of gases that follow ideal gas law in all conditions is:

- A. 0
- B. 1
- C. 2
- D. 3
- E. Infinite

No gas is an ideal gas under all conditions.

Option A

#### 2.105: van der Waal's Equation

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT, \quad a > 0, b > 0$$

$P$  = Pressure

$V$  = Volume of the container in which the gas is

$n$  = number of moles = Amount of gas

$T$  is temperature measured in Kelvin

#### Example 2.106

Solve van der Waal's equation for  $P$ .

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

Divide both sides by  $V - nb$ :

$$P + a \frac{n^2}{V^2} = \frac{nRT}{V - nb}$$

Subtract  $a \frac{n^2}{V^2}$  from both sides:

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}$$

### Example 2.107: Optional/Calculus

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}$$

Find the partial derivative of the above with respect to  $V$ . A partial means that  $V$  is variable and everything else ( $n, R, T, a, b$ ) is constant.

Rewrite the equation by moving the terms to the numerator:

$$P = nRT(V - nb)^{-1} - an^2V^{-2}$$

Differentiate both sides with respect to  $V$ , and use the chain rule:

$$\frac{\partial P}{\partial V} = nRT(-1)(V - nb)^{-2} \frac{d}{dV}(V - nb) - (-2)(an^2)(V^{-3})$$

Move the negative exponent terms back to the denominator:

$$\frac{\partial P}{\partial V} = -\frac{nRT}{(V - nb)^2} + \frac{2(an^2)}{V^3}$$

### 2.108: $a$ term

$a$  adjusts for the complexity of a particle and the strength of its interparticle attractions.

### Example 2.109

In van der Waals equation of state for a nonideal gas, the term that accounts for intermolecular forces is:

- A.  $(V - b)$
- B.  $\left(p + \frac{a}{V^2}\right)$
- C.  $RT$
- D.  $(RT)^{-1}$  (JEE Advanced 1988)

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

Substitute  $n = 1$ :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

The  $a$  term adjusts for strength of interparticle attractions / intermolecular forces

*Option B*

### 2.110: $a$ term

As  $a$  increases, liquefaction occurs more easily.

If  $a$  increases, the interparticle attractions increase.

Since liquefying the gas requires having the particle closer and attracted, liquefaction becomes easier.

$a$  increases  $\Rightarrow$  interparticle attractions increase

### Example 2.111

The values of van der Waals constant  $a$  for the gases  $O_2$ ,  $N_2$ ,  $NH_3$  and  $CH_4$  are 1.360, 1.390, 4.170 and 2.253  $L^2 \text{ atm mol}^{-2}$  respectively. The gas which can most easily be liquefied is:

- A.  $O_2$
- B.  $N_2$
- C.  $NH_3$
- D.  $CH_4$  (JEE Advanced 1989)

Option C

### 2.112: $b$ term

$b$  adjusts for the volume taken up by a particle.

Total Volume =  $V$

The numerical value of  $b$  is the four times the actual volume occupied by the molecules in 1 mole of the gas

$$b = N_A \left[ 4 \left( \frac{4}{3} \pi r^3 \right) \right], r = \text{radius of molecule of the gas}$$

### Example 2.113

In van der Waals equation of state of the gas law, the constant  $b$  is a measure of:

- A. Volume occupied by the molecules
- B. Intermolecular attractions
- C. Intermolecular repulsions
- D. Intermolecular repulsions per unit volume (JEE Main 2004)

Option A

### Example 2.114

If we assume  $a = 0$ ,  $b = 0$  then the real gas equation becomes \_\_\_\_\_

$$\left( P + 0 \cdot \frac{n^2}{V^2} \right) (V - n \cdot 0) = nRT$$

$$PV = nRT$$

Ideal gas equation

### Example 2.115

$$\underbrace{\left( P + a \frac{n^2}{V^2} \right)}_{\text{Pressure Term}} \underbrace{(V - nb)}_{\text{Volume Term}} = nRT$$

A. Term with $a$	1. Increases	I. Pressure
B. Term with $b$	2. Decreases	II. Volume

In the real gas equation, there are terms with  $a$  and  $b$ . Match the term with its effect in the equation.

$$A - 1 - I$$
$$B - 2 - II$$

### 2.116: Non-Ideal Gases

The ideal gas equation does not hold when pressure is high and temperature is low since the molecules come close to each other, and intermolecular forces of attraction between molecules become relevant.

Boiling point of a liquid is the point at which the liquid become a gas. Molecular forces of attraction are stronger in liquids than in gases.

If the temperature is low enough to be close to the boiling point of a gas, its behaviour will deviate from ideal gas behaviour.

### Example 2.117

When does a gas deviate the most from its ideal behaviour?

- A. At low pressure and low temperature
- B. At low pressure and high temperature
- C. At high pressure and low temperature
- D. At high pressure and high temperature (JEE Main, April 11, 2015)

*Option C*

### Example 2.118

Van der Waals equation for a gas is stated as  $P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$ . The equation reduces to the perfect gas equation  $P = \frac{nRT}{V}$  when:

- A. Temperature is sufficiently high and pressure is low
- B. Temperature is sufficiently low and pressure is high
- C. Both temperature and pressure are very high
- D. Both temperature and pressure are very low (JEE Main, April 9, 2015)

*Option A*

## B. Compressibility Factor

### 2.119: Molar Volume

The volume of one mole of gas is molar volume

$$V_m = \frac{V}{n}$$

Where

$V$  = volume of gas  
 $n$  = moles of gas

$$V_m = \frac{V}{n} \Rightarrow V = nV_m$$

### Example 2.120

A container of capacity 5L contains 20 moles of oxygen gas. Find the molar volume.

Molar volume

$$= \text{Volume occupied by one mole} = V_m = \frac{V}{n} = \frac{5}{20} = \frac{1}{4} \text{ L}$$

### 2.121: van der Waal's Equation for one Mole

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT, \quad a > 0, b > 0$$

$P$  = Pressure

$V_m$  = Molar Volume

$n$  = number of moles = Amount of gas

$T$  is temperature measured in Kelvin

The real gas equation is:

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT, \quad a > 0, b > 0$$

Substitute  $V = nV_m$ :

$$\begin{aligned} \left(P + a \frac{n^2}{n^2 V_m^2}\right)(nV_m - nb) &= nRT \\ \left(P + \frac{a}{V_m^2}\right)(V_m - b)n &= nRT \end{aligned}$$

Divide both sides by  $n$ :

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

### Example 2.122

In ideal gas law, for gas of one mole,  $Z = \frac{PV}{nRT} = 1$  (where  $Z$  is comp)

### 2.123: $Z$ = Compressibility Factor for Ideal Gas

For an ideal gas of quantity one mole:

$$Z = \frac{PV}{RT} = 1$$

$$PV = RT$$

$$\frac{PV}{RT} = 1$$

### 2.124: $Z$ = Compressibility Factor for Real Gas

For a real gas,  $Z$  does not have to be 1. It can be more than 1, or less than one.

$$Z = \frac{PV}{RT} = \frac{V_{Real}}{V_{Ideal}}$$

If:

$Z < 1$ : The volume of the real gas is less than the volume of an equivalent quantity of ideal gas.

$Z > 1$ : The volume of the real gas is greater than the volume of an equivalent quantity of ideal gas.

$Z = 1$ : The gas behaves like an ideal gas.

$$Z = \frac{PV}{RT} = \frac{P_{\text{Real}}V_{\text{Real}}}{RT_{\text{Real}}}$$

$$\text{Substitute } 1 = \frac{P_{\text{Ideal}}V_{\text{Ideal}}}{RT_{\text{Ideal}}} = \frac{RT_{\text{Ideal}}}{P_{\text{Ideal}}V_{\text{Ideal}}}$$

$$Z = \frac{P_{\text{Real}}V_{\text{Real}}}{RT_{\text{Real}}} \times \frac{RT_{\text{Ideal}}}{P_{\text{Ideal}}V_{\text{Ideal}}}$$

To compare real with ideal, make the temperature and pressure the same:

$$P = P_{\text{Real}} = P_{\text{Ideal}}, \quad T = T_{\text{Real}} = T_{\text{Ideal}}$$

$$Z = \frac{PV_{\text{Real}}}{RT} \times \frac{RT}{PV_{\text{Ideal}}}$$

Which simplifies to:

$$Z = \frac{V_{\text{Real}}}{V_{\text{Ideal}}}$$

### Example 2.125

The compression factor of a gas is less than unity at STP. Therefore:

- A.  $V_m > 22.4 \text{ L}$
- B.  $V_m < 22.4 \text{ L}$
- C.  $V_m = 22.4 \text{ L}$
- D.  $V_m \geq 44.8 \text{ L}$  (JEE Advanced 2000)

$$Z < 1$$

$$\frac{V_{\text{Real}}}{V_{\text{Ideal}}} < 1$$

$$\frac{V_{\text{Real}}}{22.4 \text{ L}} < 1$$

$$V_{\text{Real}} < 22.4$$

Option B

### 2.126: Z for low pressure

$$Z = \frac{PV}{RT} = 1 - \frac{a}{VRT} < 1$$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressure, volume is very large. Hence, the  $b$  term can be neglected.

$$V - b \approx V$$

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

Divide both sides by  $RT$ :

$$\frac{PV}{RT} + \frac{a}{VRT} = 1$$

$$\frac{PV}{RT} = 1 - \frac{a}{VRT}$$

### Example 2.127

*Mark the correct option*

If  $Z$  is a compressibility factor, van der Waals equation for low pressure can be written as:

- A.  $Z = 1 + \frac{RT}{Pb}$
- B.  $Z = 1 - \frac{a}{VRT}$
- C.  $Z = 1 - \frac{Pb}{RT}$
- D.  $Z = 1 + \frac{Pb}{RT}$  (JEE Main 2014)

*Option B*

### 2.128: $Z$ for high pressure

$$Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT} > 1$$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At high pressure, pressure is much greater than  $\frac{a}{V^2}$ . Hence, the  $a$  term can be neglected.

$$P + \frac{a}{V^2} \approx P$$

$$P(V - b) = RT$$

$$PV - Pb = RT$$

Divide both sides by  $RT$ :

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

### Example 2.129

*Mark the correct option*

At very high pressures, the compressibility factor of one mole of a gas is given by::

- A.  $1 + \frac{Pb}{RT}$
- B.  $\frac{Pb}{RT}$
- C.  $1 - \frac{Pb}{RT}$
- D.  $1 - \frac{b}{VRT}$  (JEE Main 2012; JEE Main April 9, 2016)

## C. Critical Definitions



### 2.130: Critical Temperature

Critical temperature is the maximum temperature at which a gas can be liquefied. That is the temperature above which a liquid cannot exist.

$$T_c = \left(\frac{8}{27R}\right)\left(\frac{a}{b}\right)$$

- A substance becomes a liquid due to intermolecular forces of attraction dominating.
- If the temperature is increased to the critical temperature, the kinetic energy of the molecules increases, and the molecules move around very fast, and the intermolecular forces are not sufficient to convert the substance into a liquid.

### Example 2.131

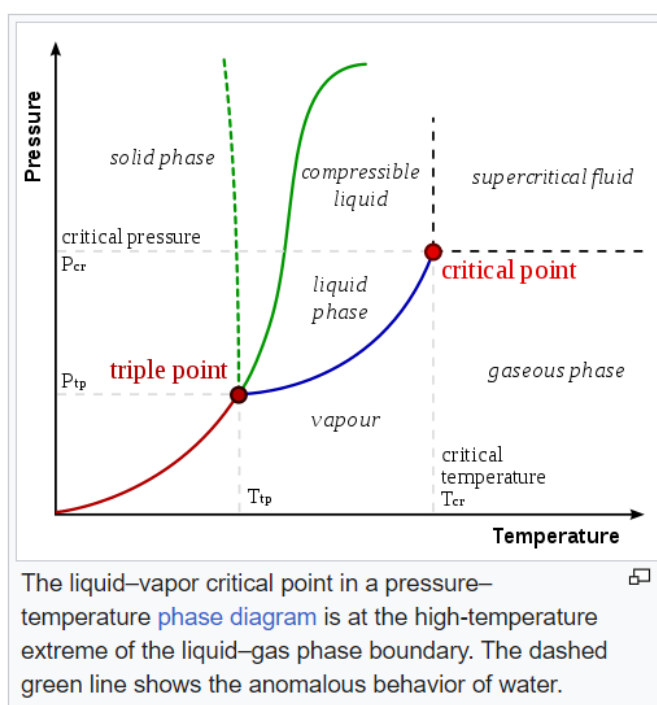
Critical temperature for oxygen is  $-118.6^\circ\text{C}$ . Interpret this statement.

Above  $-118.6^\circ\text{C}$ , oxygen will be in the gaseous state, not in the liquid or solid state.

### 2.132: Critical Pressure

Critical pressure is the minimum pressure required to cause liquefaction at critical temperature

$$P_c = \left(\frac{1}{27}\right)\frac{a}{b^2}$$



- If a substance is above its critical temperature, it cannot be liquefied.
- At the critical temperature, a substance will be liquid for some pressures and gaseous for other pressures. The minimum pressure for which the substance will be liquid at critical temperature is critical pressure.

### 2.133: Critical Volume

Critical volume is the volume occupied by one mole of gas at critical temperature and critical pressure.

$$V_c = 3b$$

### 2.134: Critical State

A gas at critical temperature, critical pressure and critical volume is in critical state.

$$\frac{P_c V_c}{RT_c} = \frac{3}{8}$$

## D. Virial Equation

### Example 2.135

Solve the equation below for  $P$ :

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT, \quad a > 0, b > 0$$

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT, \quad a > 0, b > 0$$

Divide both sides by  $V_m - b$ :

$$P + \frac{a}{V_m^2} = \frac{RT}{V_m - b}$$

Isolate  $P$ :

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

### 2.136: $Z$

$$Z = \frac{PV_m}{RT} = 1 + \left(b - \frac{a}{RT}\right)\left(\frac{1}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \dots$$

Substitute  $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$  in  $Z = \frac{PV_m}{RT} = PV_m \left(\frac{1}{RT}\right)$ :

$$Z = \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right)V_m \left(\frac{1}{RT}\right)$$

Simplify and rearrange:

$$= \frac{V_m}{V_m - b} - \frac{a}{V_m RT} = \frac{1}{\frac{V_m - b}{V_m}} - \frac{a}{V_m RT} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{V_m RT}$$

$\frac{1}{1 - \frac{b}{V_m}}$  is the sum of a geometric series with  $a = 1, r = \frac{b}{V_m} \Rightarrow S = \frac{1}{1 - \frac{b}{V_m}} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \dots$

$$= \left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \dots\right] - \frac{a}{V_m RT}$$

Rearrange<sup>4</sup> and move the  $-\frac{a}{V_m RT}$  to earlier, and factor

$$= 1 + \left(b - \frac{a}{RT}\right)\left(\frac{1}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \dots$$

<sup>4</sup> We can rearrange since it is a finite geometric series, and hence convergent. If it were divergent, we could not rearrange.

### Example 2.137

Explain why  $\frac{b}{V_m} < 1$

$b$  is 4 times the volume taken up by the gas particles of one mole

$V_m$  is the volume that the gas occupies.

In a gas, the particles are far apart, and hence

$$\frac{b}{V_m} < 1$$

### 2.138: Boyle Temperature

At the Boyle temperature a real gas behaves like an ideal gas over a wide range of pressures.

$$T_B = \frac{a}{Rb}$$

$$1 + \left(b - \frac{a}{RT}\right)\left(\frac{1}{V_m}\right) + \left(\frac{b}{V_m}\right)^2 + \dots$$
$$b - \frac{a}{RT_B} = 0$$
$$b = \frac{a}{RT_B}$$
$$T_B = \frac{a}{Rb}$$

65. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is

(a) critical temperature

(b) Boyle temperature

(c) inversion temperature

(d) reduced temperature

(1981)

(JEE Advanced 1981)

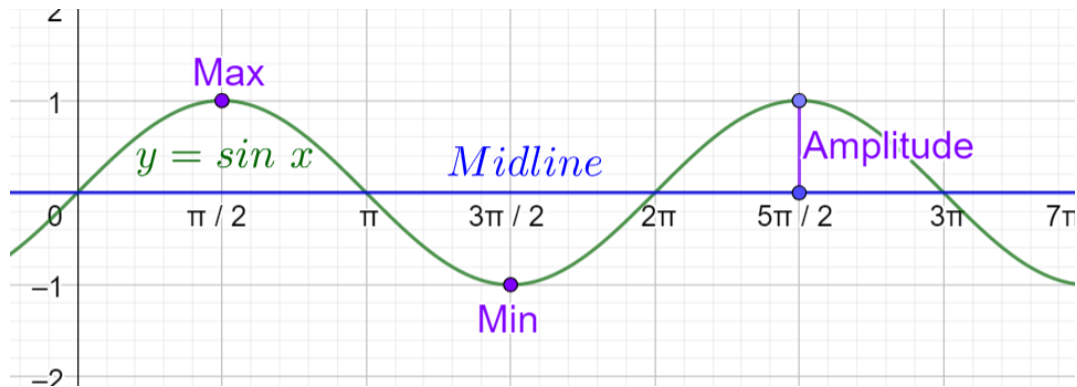
## 3. ATOMIC STRUCTURE

### 3.1 Light: Wave-Particle Duality

#### A. Waves

Waves can be of many types: sound, waves on a rope, waves in the ocean, light, etc.

#### 3.1: Sine Wave



#### 3.2: Frequency

Frequency is the number of complete waves (or cycles) that pass a given point per second.

$$\text{frequency} = \nu^5$$

Unit of frequency is

$$\text{hertz} = \frac{\text{cycles}}{\text{s}}$$

As a connection to maths:

$$\text{Frequency} = \frac{1}{\text{Period}}$$

#### 3.3: Wavelength

Wavelength is the distance between two corresponding points on a wave. For example, from crest to crest, or trough to trough.

$$\text{Period} = \text{Wavelength} = \lambda = \frac{m}{\text{cycle}}$$

#### 3.4: Amplitude

Amplitude is the difference between the midline and the crest (or midline and the trough).

- Amplitude is a scalar.

---

<sup>5</sup> This is the Greek Letter  $\nu$  =  $\nu$ . It looks very similar to the English Letter  $\nu$ .

### 3.5: Speed

The speed of a wave is

$$\text{Speed} = v \times \lambda$$

Speed of a wave is given by the number of waves that pass a point multiplied by the wavelength of each wave.

### Example 3.6

Determine the unit of speed for the formula  $\text{Speed} = v \times \lambda$  using dimensional analysis.

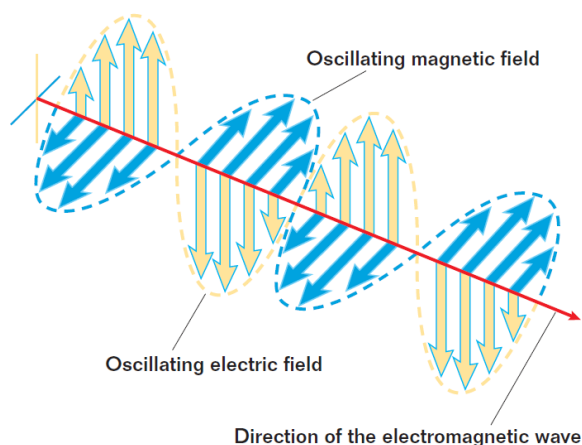
$$\text{Speed} = \frac{\text{cycles}}{\text{s}} \times \frac{\text{m}}{\text{cycle}} = \frac{\text{m}}{\text{s}}$$

## B. Electromagnetic Radiation (Waves)

For atomic structure, the waves which are relevant are electromagnetic radiation.

### 3.7: Electromagnetic Radiation

Electromagnetic radiation is energy propagated by electric and magnetic fields at right angles to each other.



### 3.8: Electromagnetic Spectrum

Electromagnetic radiation across the range of possible frequencies is called the electromagnetic spectrum. Every part of the electromagnetic spectrum has important real-life applications.

Some patterns to note:

- As you go down the chart, the wavelength ( $\lambda$ ) decreases and frequency ( $f$ ) increases.

Classification	Range	Applications
radio waves	$\lambda > 30 \text{ cm}$ $f < 1.0 \times 10^9 \text{ Hz}$	AM and FM radio; television
microwaves	$30 \text{ cm} > \lambda > 1 \text{ mm}$ $1.0 \times 10^9 \text{ Hz} < f < 3.0 \times 10^{11} \text{ Hz}$	radar; atomic and molecular research; aircraft navigation; microwave ovens
infrared (IR) waves	$1 \text{ mm} > \lambda > 700 \text{ nm}$ $3.0 \times 10^{11} \text{ Hz} < f < 4.3 \times 10^{14} \text{ Hz}$	molecular vibrational spectra; infrared photography; physical therapy
visible light	$700 \text{ nm (red)} > \lambda > 400 \text{ nm (violet)}$ $4.3 \times 10^{14} \text{ Hz} < f < 7.5 \times 10^{14} \text{ Hz}$	visible-light photography; optical microscopy; optical astronomy
ultraviolet (UV) light	$400 \text{ nm} > \lambda > 60 \text{ nm}$ $7.5 \times 10^{14} \text{ Hz} < f < 5.0 \times 10^{15} \text{ Hz}$	sterilization of medical instruments; identification of fluorescent minerals
X rays	$60 \text{ nm} > \lambda > 10^{-4} \text{ nm}$ $5.0 \times 10^{15} \text{ Hz} < f < 3.0 \times 10^{21} \text{ Hz}$	medical examination of bones, teeth, and vital organs; treatment for types of cancer
gamma rays	$0.1 \text{ nm} > \lambda > 10^{-5} \text{ nm}$ $3.0 \times 10^{18} \text{ Hz} < f < 3.0 \times 10^{22} \text{ Hz}$	examination of thick materials for structural flaws; treatment of types of cancer; food irradiation

### 3.9: Speed of Electromagnetic Radiation

The speed of electromagnetic radiation in vacuum is

$$c = \nu \times \lambda$$

$$c \approx 3 \times 10^8 \frac{\text{m}}{\text{s}} = 3 \times 10^{17} \frac{\text{nm}}{\text{s}}$$

- Speed of electromagnetic radiation is always a constant, irrespective of your frame of reference.
- Relative velocity concepts from classical mechanics (kinematics) do not apply to the speed of electromagnetic radiation.

#### Example 3.10

- The value of Planck's constant is  $6.63 \times 10^{-34} \text{ J}$ . The speed of light is  $3 \times 10^{17} \frac{\text{nm}}{\text{s}}$ . What is the wavelength in nanometer of a quantum of light with frequency of  $6 \times 10^{15} \text{ s}^{-1}$ ? (**NEET 2013**)
- The value of Planck's constant is  $6.63 \times 10^{-34} \text{ J}$ . The velocity of light is  $3.0 \times 10^8 \frac{\text{m}}{\text{s}}$ . What is the wavelength in nanometers of a quantum of light with frequency of  $8 \times 10^{15} \text{ s}^{-1}$

#### Part A

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{17}}{6 \times 10^{15}} = \frac{300}{6} = 50 \text{ nm}$$

#### Part B

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{17}}{8 \times 10^{15}} = 37.5 \text{ nm}$$

### 3.11: Proportionality

For electromagnetic radiation in vacuum, the frequency and the wavelength are inversely proportional, since the speed is a constant.

$$\nu \propto \frac{1}{\lambda}$$

$$c = \nu \times \lambda$$

$$v = \frac{c}{\lambda}$$
$$v \propto \frac{1}{\lambda}$$

## C. Light as a Wave

We consider the characteristics that differentiate waves from matter. And then we see the features of electromagnetic radiation.

### 3.12: Change of Medium: Refraction

When a light wave passes from one medium to another, it has an abrupt change in direction. This is a feature of waves.

A particle does not undergo refraction.

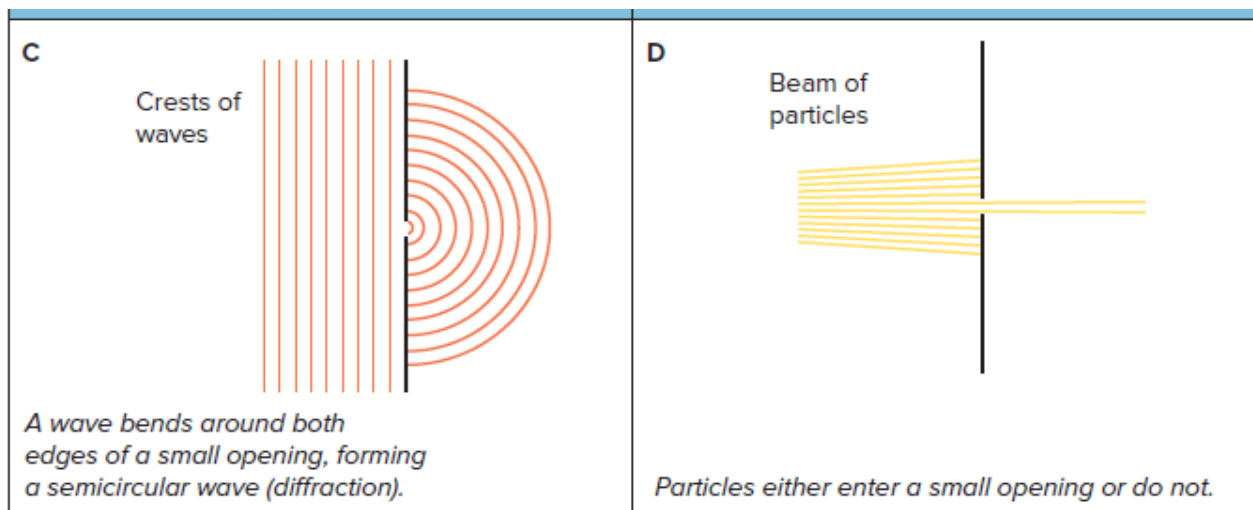
### 3.13: Change of Medium: Dispersion

When a light wave enters a prism, it disperses (separates) into its constituent colors.

A particle does not undergo dispersion.

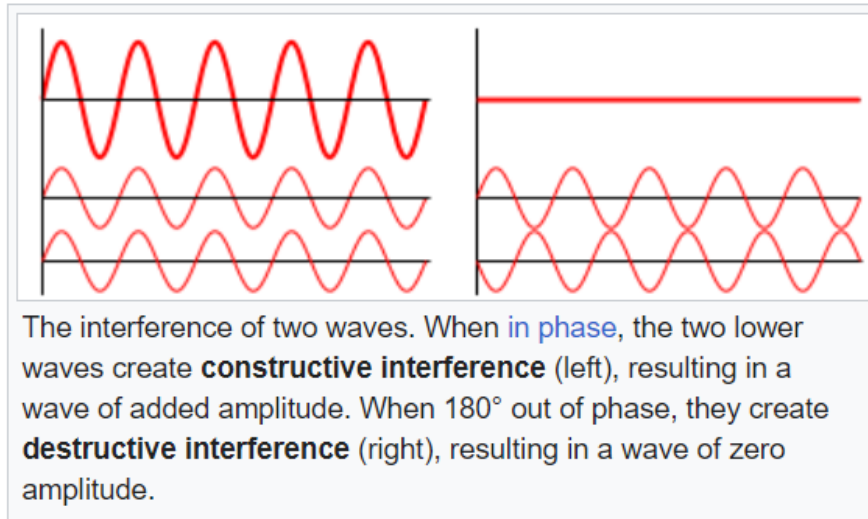
### 3.14: Diffraction

When a wave strikes the edge of an object it bends around it. In particular, if the size of the slit is roughly equal to the wavelength, it forms a semi-circular wave on the other side.



### 3.15: Interference

When two waves are incident at the same point, the amplitude at that point is equal to the vector sum of the amplitudes of the individual waves.



Perfect *constructive interference* occurs when two waves with the same wavelength are exactly in phase. The amplitude of the result is double the amplitude of the input waves.

Perfect *destructive interference* occurs when two waves with the same wavelength are exactly  $180^\circ = \pi$  out of phase. The overall result is that the two waves completely cancel.

Interference can also be something between perfectly constructive and perfectly destructive. The resulting wave will depend on the parameters of the two input waves.

### 3.16: Diffraction and Interference for Light

Light exhibits diffraction and hence behaves like a wave.

Light exhibits interference and hence behaves like a wave.

## D. Electromagnetic Radiation as a Particle/Blackbody Radiation

Around a hundred years ago, when light was considered a wave, there was evidence to the contrary, which showed that the wave model was not sufficient to explain the behaviour of light.

### 3.17: Math Revision: Continuous versus discrete variables

Continuous variables can take on any real value.

Discrete variables can only take on only specified values.

- Number of people attending a party is a discrete variable.  $\pi$  people cannot attend a party.
- Weight of a person, mass of a substance, etc is a continuous variable.

### 3.18: Blackbody Radiation

A heated object emits light. As the temperature goes higher, the frequency of the light reduces.

Classical wave model cannot explain this behaviour. Waves are infinitely divisible. So, energy should be radiated equally across all parts of the electromagnetic spectrum.

However, this is against observations.

- Consider iron at room temperature, it does not emit.



- Consider iron is heated (consider molten iron), it emits visible light.

### 3.19: Quantization of Electromagnetic Radiation

Quantization was postulated by Max Planck as a way to explain the problem with blackbody radiation.

Energy can only be emitted in certain quantities.

Atoms have energy only in certain quantities.

Each quantity is an energy packet, called a quantum of energy (*plural: quanta*).

It takes on the attribute of particles.

### 3.20: Quantum Theory

$$E = nh\nu$$

Where

$E = \text{energy of the radiation}$

$n \in \mathbb{N}$  is a quantum number

$\nu = \text{frequency}$

Planck's constant  $= h \approx 6.626 \times 10^{-34} \text{ J}$

Things to note:

- In absolute terms the value of  $h$  is very small.
- $\nu$  is a part of the equation. We are treating it like a wave.
- $n$  is a part of the equation. We are quantizing the equation and forcing it to behave in discrete jumps (like particles).

### 3.21: Energy State of an Atom

An atom changes its energy state by emitting (or absorbing) one or more quanta of energy.

### 3.22: Minimum change in Energy State

Because of quantization, energy is not infinitely divisible, and instead must change in discrete steps. The minimum change in energy is:

$$\text{Min}(\Delta E) = h\nu = \frac{hc}{\lambda}$$

Since

$$\Delta E = E_{\text{New}} - E_{\text{Old}} = n_{\text{New}}h\nu - n_{\text{Old}}h\nu = \Delta n h\nu$$

$$n \in \mathbb{N} \Rightarrow \Delta n \in \mathbb{N} \Rightarrow \text{Min}(\Delta n) = 1$$

Substitute  $\Delta n = 1$

$$\text{Min}(\Delta E) = h\nu$$

Substitute  $\nu = \frac{c}{\lambda}$ :

$$\text{Min}(\Delta E) = \frac{hc}{\lambda}$$

### Example 3.23

Calculate the energy in joule corresponding to light of wavelength 45 nm. (Planck's constant,  $h = 6.63 \times 10^{-34} \text{ J}$ , speed of light,  $c = 3 \times 10^8 \frac{\text{m}}{\text{s}}$ ) (NEET 2014)

$$E = \frac{hc}{\lambda} = 4.42 \times 10^{-18}$$

### Example 3.24

For given energy,  $E = 3.03 \times 10^{-19}$  joules corresponding wavelength in  $nm$  is ( $h = 6.626 \times 10^{-34} J, c = 3 \times 10^8 \frac{m}{s}$ ) (NEET 2000)

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3.03 \times 10^{-19}} = \frac{662.6}{1.01} nm$$

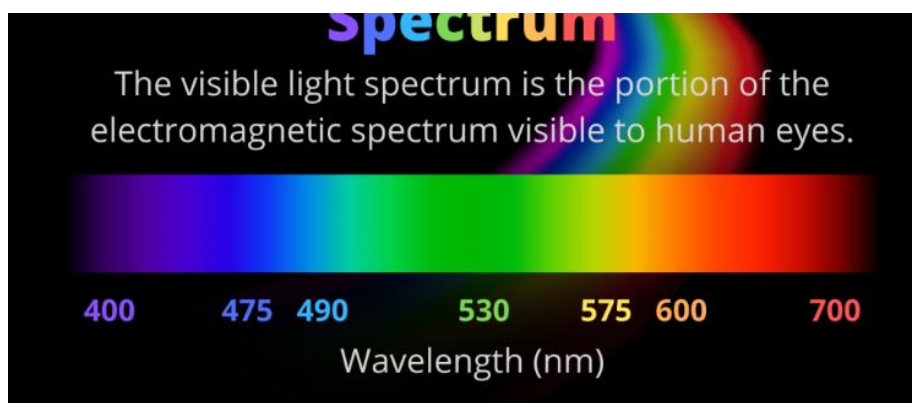
### Example 3.25

The energies  $E_1$  and  $E_2$  of two radiations are 25 eV and 50 eV respectively. The value of  $\lambda_1$  in terms of  $\lambda_2$  will be (NEET 2011)

$$\frac{E_1}{E_2} = \frac{\frac{hc}{\lambda_1}}{\frac{hc}{\lambda_2}} = \frac{hc}{\lambda_1} \cdot \frac{\lambda_2}{hc} = \frac{\lambda_2}{\lambda_1} = \frac{25}{50} = \frac{1}{2}$$
$$\lambda_1 = 2\lambda_2$$

## E. Photoelectric Effect

The photoelectric effect is the second place where the classical wave model failed to describe reality.



### 3.26: Classical Wave Theory

The amplitude of a light source is related to its brightness (or intensity). A brighter source has light of higher amplitude.

The color of a light source is related to its frequency. For example, red is the lowest visible frequency, and violet is the highest visible frequency.

In classical wave theory, the amplitude is related to the intensity of a wave. For example, consider an ocean wave with a height of 3 inches, and another with a height of 3 feet. The second wave has greater intensity.

### 3.27: Photoelectric effect

When light above a minimum (*threshold*) frequency shines on a metal plate, a current flows in the metal without a *time lag*.

The threshold frequency depends on the metal.

### 3.28: Threshold Frequency

Threshold frequency is in disagreement with classical wave theory.

### 3.29: Absence of time lag

Absence of time lag is in disagreement with classical wave theory.

## F. Light Particle: Photons

### 3.30: Photons

Light particles are called photons. Atoms change energy when they absorb or emit photons.

- Intensity is related to number of photons.
- Energy =  $h\nu$  is proportional to frequency and inversely proportional to wavelength

Photon of minimum energy = *minimum frequency* is required to free an electron.

Photon of lower frequency is not sufficient to free electrons.

Energy cannot be saved up. It is quantized. Hence, there is no time lag.

## 3.2 Bohr Model: Hydrogen Atom

### A. Line Spectra

#### 3.31: Line Spectra

If the light from electrically excited gases is refracted, it does not decompose into all the colors of the rainbow. Instead, it creates a line spectrum: light of specific wavelengths.

#### 3.32: Application: Fluorescent Lights

When mercury vapor in the light is excited, it releases electromagnetic radiation at a specific frequency, which then causes a phosphor coating to glow.

### B. Bohr Model

This is a model for the hydrogen atom, which works for the hydrogen, and some hydrogen-like atoms, but cannot be generalized.

#### 3.33: Bohr Model of the Atom

H atom has fixed energy levels, called stationary state. Each state corresponds to a fixed circular orbit of the electron around the nucleus.

### 3.34: Quantum Number and Orbits

$n$  is a natural number

When  $n = 1$ , the electron is in lowest orbit, also called ground state.

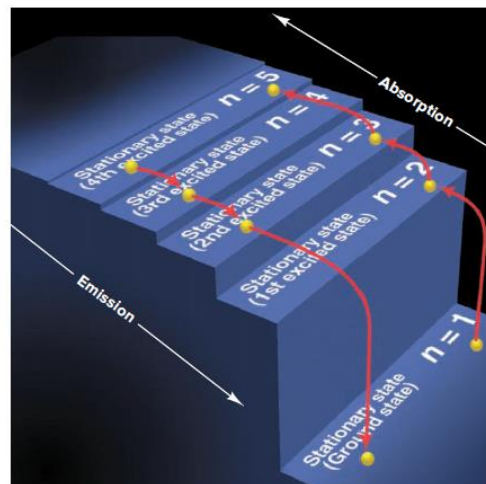
When  $n > 1$ , the electron is in excited state, and further from the nucleus.

### 3.35: Orbits

- Increase in energy level of electron corresponds to higher orbit.
- Decrease in energy level of electron corresponds to lower orbit.

### 3.36: Change in Orbits

- Change in energy happens only with change in orbit.
- Change in energy requires emission or absorption of a photon.



**Figure 7.10** A quantum “staircase” as an analogy for atomic energy levels. Note that the electron can move up or down one or more steps at a time but cannot lie between steps.

$$E_{\text{photon}} = \Delta E_{\text{atom}} = E_{\text{final}} - E_{\text{initial}} = h\nu$$

### 3.37: Line Spectra

Emission or absorption can only happen with change in orbit.

$\Delta E_{\text{atom}}$  is fixed

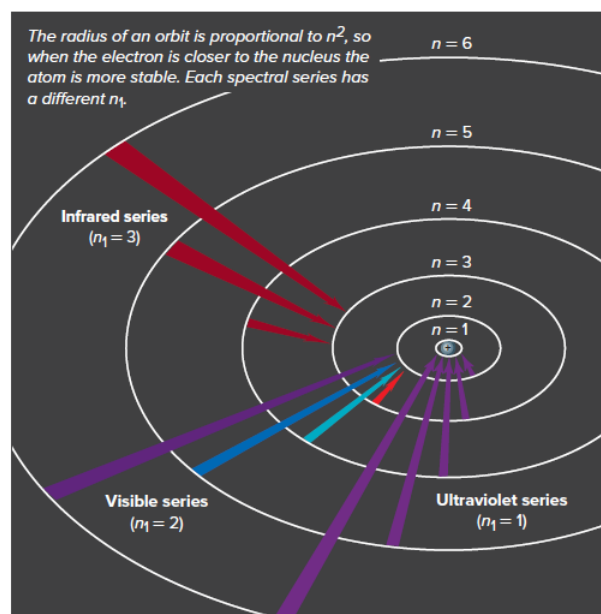
Hence, photons emitted must be of those frequencies only.

#### Example 3.38

An electron in excited state at  $n = 5$  drops to ground state at  $n = 1$ .

- What happens to the energy of the electron?
- What happens to the rest of the energy?

*Electron energy reduces  
 Rest of the energy is emitted as a photon*



### 3.39: Names of the Line Spectra for Hydrogen

The groups of line spectra for hydrogen are important enough to have names.

**Table 2.3 The Spectral Lines for Atomic Hydrogen**

Series	$n_1$	$n_2$	Spectral Region
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

For example:

- A transition from  $n = 1$  to a value of  $n = 2,3, \dots$  is called Lyman Series, and the associated radiation will be in the ultraviolet region of the electromagnetic spectrum.
- A transition from  $n = 3$  to  $n = 1$  is also Lyman series.

### Example 3.40

Which of the following series of transitions in the spectrum of hydrogen atom falls in visible region?

- A. Brackett series
- B. Lyman series
- C. Balmer series
- D. Paschen series (NEET 2019)

Option C

## C. Energy of an Orbit

### 3.41: Bohr Energy of an Orbit

The Bohr energy of an orbit of a *single atom* is:

$$E_n = -K \left( \frac{Z}{n} \right)^2$$

Where

$$K = \text{Constant} = 2.18 \times 10^{-18} \text{ J}$$

$$Z = \text{Charge of the nucleus}$$

$$n = \text{Orbit Number}$$

It can also be expressed per mole rather than per atom.

### 3.42: Bohr Energy of Hydrogen Atom

$$E_n = -\frac{K}{n^2}$$

Substitute  $Z = 1$  in  $E_n = -K \left( \frac{Z}{n} \right)^2$

$$E_n = -\frac{K}{n^2}$$

### Example 3.43

The energy of second Bohr orbit of the hydrogen atom is  $-328 \text{ kJ mol}^{-1}$ ; hence the energy of fourth Bohr orbit would be (NEET 2005)

$$E_2 = -K \left( \frac{1}{2} \right)^2 = -\frac{K}{4}$$

$$E_4 = -K \left( \frac{1}{4} \right)^2 = -\frac{K}{16}$$

$$E_4 = \frac{E_2}{4} = -\frac{328}{4} = -82 \frac{kJ}{mol}$$

### 3.44: Change in Energy

If an electron changes the orbit, the change in energy can be measured using:

$$\Delta E = -K \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The change in energy is equal to the energy of the old orbit minus energy of the new orbit:

$$\Delta E = \underbrace{E_{n_1}}_{\text{New Orbit}} - \underbrace{E_{n_2}}_{\text{Old Orbit}} = -\frac{K}{n_1^2} - \left( -\frac{K}{n_2^2} \right) = -K \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

### 3.45: erg

$$10^7 \text{ erg} = 1 \text{ J}$$

The erg is a unit of energy used for small values of energy.

1

### Example 3.46

In a Bohr's model of an atom, when an electron jumps from  $n = 1$  to  $n = 3$ , how much energy will be emitted or absorbed?

- A.  $2.389 \times 10^{-12}$  ergs
- B.  $0.239 \times 10^{-10}$  ergs
- C.  $2.15 \times 10^{-11}$  ergs
- D.  $0.1936 \times 10^{-10}$  ergs (NEET 1996)

$$\begin{aligned} \Delta E &= K \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = K \left( \frac{1}{1} - \frac{1}{9} \right) = K \left( \frac{8}{9} \right) \\ &= 2.18 \times 10^{-18} \left( \frac{8}{9} \right) \times 10^7 \text{ ergs} \\ &= 2.18 \left( \frac{8}{9} \right) \times 10^{-11} \text{ ergs} \\ &= 1.94 \times 10^{-11} \text{ ergs} \\ &= 0.194 \times 10^{-10} \text{ ergs} \\ &\text{Option D} \end{aligned}$$

### 3.47: Change in Energy

$$\Delta E \propto \frac{1}{n_1^2} - \frac{1}{n_2^2}$$

$$\begin{aligned} \Delta E &= -\frac{K}{n_2^2} + \frac{K}{n_1^2} = K \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ \Delta E &= K \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \end{aligned}$$

$$\Delta E \propto \frac{1}{n_1^2} - \frac{1}{n_2^2}$$

### 3.48: Minimizing $\Delta E$

To minimize  $\Delta E$ ,

- $n_1$  will be maximum (*Higher priority condition*)
- $n_2$  will be minimum (*Lower priority condition*)

### Example 3.49

According to the Bohr theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon?

- A.  $n = 6$  to  $n = 1$
- B.  $n = 5$  to  $n = 4$
- C.  $n = 6$  to  $n = 5$
- D.  $n = 5$  to  $n = 3$  (NEET 2011)

$n_2 > n_1$   
 $n_1$  should be max  
 $n_2$  should be min  
*Option C*

$$x = \frac{1}{5^2} - \frac{1}{4^2} = \frac{1}{25} - \frac{1}{16}$$

$$y = \frac{1}{6^2} - \frac{1}{5^2} = \frac{1}{36} - \frac{1}{25}$$

$$x - y = \frac{1}{25} - \frac{1}{16} - \left( \frac{1}{36} - \frac{1}{25} \right) = \frac{2}{25} - \frac{1}{16} - \frac{1}{36} > 0$$

$x - y > 0$   
 $x > y$

2

### 3.50: Maximizing $\Delta E$

To maximize  $\Delta E$ ,

- $n_1$  will be minimum (*Higher priority condition*)
- $n_2$  will be maximum (*Lower priority condition*)

3

### 3.51: Ionization Energy

Moving an electron from  $n = 1$  to  $n = \infty$  is equivalent to removing it from the atom altogether.

This process is called ionization.

The energy required for this process (*ionization energy*)

$$= K = 2.18 \times 10^{-18} \text{ J}$$

Substitute  $\text{Min}(n_1) = 1, \text{Max}(n_2) = \infty$

<sup>6</sup> For those who know Calculus, we are applying the limit as  $n_2 \rightarrow \infty$

$$\Delta E = K \left( \frac{1}{1} - \frac{1}{\infty} \right) = K \left( \frac{1}{1} - 0 \right) = K = 2.18 \times 10^{-18} \text{ J}$$

4

### Example 3.52

Mark the correct option

Based on equation  $E_n = -2.18 \times 10^{-18} \text{ J} \left( \frac{Z}{n} \right)^2$  certain conclusions are written. Which of them is not correct?

- A. Equation can be used to calculate the change in energy when the electron changes orbit.
- B. For  $n = 1$ , the electron has a more negative energy than it does for  $n = 6$  which means that the electron is more loosely bound in the smallest allowed orbit.
- C. The negative sign in equation simply means that the energy of electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.
- D. Larger the value of  $n$ , the larger is the orbit radius. (NEET 2013)

Option B

## D. Rydberg Equation

### 3.53: Rydberg Equation: Empirical

The Rydberg equation was proposed based on empirical data, not a mathematical model. Later on, it was justified using the Bohr model.

### 3.54: Rydberg Equation

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), n_2 > n_1$$

$$\begin{aligned} E_n &= -\frac{K}{n^2} \\ \Delta E &= E_{n_2} - E_{n_1} \\ \Delta E &= -\frac{K}{n_2^2} + \frac{K}{n_1^2} = K \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \end{aligned}$$

Substitute  $\Delta E = \frac{hc}{\lambda}$ :

$$\frac{hc}{\lambda} = K \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Solve for  $\frac{1}{\lambda}$ :

$$\frac{1}{\lambda} = \frac{K}{hc} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Substitute  $\frac{K}{hc} = R$ :

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$



### 3.55: Rydberg Constant

$$109677 \text{ cm}^{-1} \approx 1.1 \times 10^5 \text{ cm}^{-1}$$

$$= \frac{-2.18 \times 10^{-18} \text{ J}}{(\quad)(\quad)}$$

$$= \frac{-2.18 \times 10^{-18} \text{ J}}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s}) \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right)}$$

$$= 1.0967 \times 10^7 \text{ m}^{-1} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

### Example 3.56

What will be the longest wavelength line in Balmer series of spectrum?

- A. 546 nm
- B. 656 nm
- C. 566 nm
- D. 556 nm (NEET 1996)

The equation for wavelength is:

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), n_2 > n_1$$

Because it is Balmer series:

$$n_1 = 2$$

Longest wavelength means lowest energy, which means:

$$R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ should be min} \Rightarrow \frac{1}{n_2^2} \text{ should be max} \Rightarrow n_2 \text{ should be min}$$

Substitute  $n_1 = 2, n_2 = 3$ :

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{1}{2^2} - \frac{1}{3^2} = \frac{1}{4} - \frac{1}{9} = \frac{9}{36} - \frac{4}{36} = \frac{5}{36}$$

Substitute  $R \approx 1.1 \times 10^5 \text{ cm}^{-1}$ :

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = (1.1 \times 10^5 \text{ cm}^{-1}) \left( \frac{5}{36} \right)$$

$$\lambda = \frac{36}{1.1 \times 10^5 \cdot 5} \text{ cm} = \frac{36}{1.1 \times 10^5 \cdot 5} \times 10^7 \text{ nm} = \frac{36}{5.5} \times 10^2$$

$$\frac{36}{6} = 6 \Rightarrow \frac{36}{5.5} > 6$$

Option B

### E. Derivation of Bohr Model

5

### 3.57: Momentum

6

### 3.58: Angular Momentum

For a point particle:

$$l = mvr$$

7

### 3.59: Angular Momentum

$$n\lambda = 2\pi r$$

$$\lambda = \frac{h}{mv}$$

$$n\lambda = \frac{nh}{mv}$$

$$2\pi r = \frac{nh}{mv}$$

$$mvr = \frac{nh}{2\pi}$$

$$l = mvr = n\hbar$$

$$v = \frac{n\hbar}{mr}$$

8

### 3.60: Coulomb Force

$$F = k \frac{q_1 q_2}{r^2}$$

Substitute  $q_1 = Ze, q_2 = e$

$$F = \frac{Zke^2}{r^2}$$

9

### 3.61: Centripetal Force

$$\frac{mv^2}{r}$$

10

### 3.62: Radius of Bohr Orbit

$$r = \frac{n^2 \hbar^2}{Zke^2}$$

*Centripetal Force = Coulomb Force*

$$\frac{mv^2}{r} = \frac{Zke^2}{r^2}$$
$$rmv^2 = Zke^2$$

Substitute  $mvr = n\hbar \Rightarrow v = \frac{n\hbar}{mr} \Rightarrow v^2 = \frac{n^2 \hbar^2}{m^2 r^2}$

$$rm \left( \frac{n^2 \hbar^2}{m^2 r^2} \right) = Zke^2$$
$$\frac{n^2 \hbar^2}{mr} = Zke^2$$
$$r = \frac{n^2 \hbar^2}{Zke^2}$$

11

### 3.63: Radius of Orbit

$$r_n \propto \frac{n^2}{Z}$$

12

#### Example 3.64

The Bohr orbit radius for the hydrogen atom ( $n = 1$ ) is approximately  $0.530 \text{ \AA}$ . The radius for the first excited state ( $n = 2$ ) orbit is (in  $\text{\AA}$ ) (**NEET 1998**)

$$r_2 = n^2 r_1 = 4r_1 = 4(0.530) = 2.12 \text{ \AA}$$

## 3.3 Matter as a Wave

### A. Wavelength of Matter

Just as light can be considered to be a particle, matter can be considered to be a wave.

### 3.65: Matter as a Wave

$$\lambda = \frac{h}{mu}$$

$$E = mc^2$$

$$E = \frac{hc}{\lambda}$$

$$mc^2 = \frac{hc}{\lambda}$$

$$\lambda = \frac{h}{mc}$$

Since  $c$  is the speed of light, and we want to generalize this, we let  $u$  be the speed of the particle under consideration:

$$\lambda = \frac{h}{mu}$$

## B. Heisenberg's Uncertainty Principle

The position and the speed of a particle cannot be determined with complete certainty.

### 3.66: Matter as a Wave

## 3.4 Quantum Mechanical Model

### A. Quantum Numbers

#### 3.67: Principal Quantum Number $n$ :

$$n = 1, 2, 3, \dots$$

$n$  is a positive integer

It indicates size of the orbital

It indicates energy level of the atom

#### 3.68: Energy Levels/Shell

The principal quantum number gives the energy level.

#### Example 3.69

An electron has  $n = 3$ .

- A. What is its energy level?
- B. What shell is it in?

*Energy level = 3*  
*Shell 3*

#### 3.70: Azimuthal quantum number $l$ /Angular momentum quantum number $l$

$l$  is an integer from 0 to  $n - 1$

The number of possible  $l$  values is the same as the value of  $n$ .

Angular momentum number relates to the shape of the orbital.

#### Example 3.71

- A. If  $n = 3$ , determine the possible values of  $l$ .
- B. If  $n = 5$ , determine the possible values of  $l$ .
- C. If  $n = 1$ , determine the possible values of  $l$ .
- D. For a principal quantum number  $n$ , what is the number of possible  $l$  values?

#### Part A

$$l \in \{0, 1, 2\}$$

#### Part B

$$l \in \{0,1,2,3,4\}$$

Part C

$$l \in \{0\}$$

Part C

$$l \in \{0,1, \dots, n-1\} \Rightarrow n \text{ values}$$

### 3.72: Sublevels/Subshells

Each  $l$  value is designated by a letter:

- $l = 0$  is an  $s$  sublevel.
- $l = 1$  is a  $p$  sublevel.
- $l = 2$  is a  $d$  sublevel.
- $l = 3$  is an  $f$  sublevel.

The subshells are commonly referred to by letters instead of by names.  
So, a  $d$  sublevel means that  $l = 2$ .

### Example 3.73

What value of  $l$  do the following subshells have:

- A.  $2p$
- B.  $3s$

$$2p \Rightarrow l = 1$$

$$3s \Rightarrow l = 0$$

### 3.74: Magnetic Quantum Number $m$

$m$  is an integer that takes values from  $-l$  to  $l$ .

A given value of  $l$  has  $2l + 1$  values of  $m$

### Example 3.75

Determine the possible values of  $m$  if

- A.  $n = 2, l = 1$
- B.  $n = 3, l = 0$

Part A

$$m \in \{-1,0,1\}$$

Part B

$$m \in \{0\}$$

### Example 3.76

A given value of  $l$  has how many possible values of  $m$ ?

$$-l, -l + 1, \dots, 1, 0, 1, \dots, l$$

A given value of  $l$  has  $2l + 1$  values of  $m$ .

### Example 3.77

If  $n = 4, l = 3$ , what is the number of possible values of  $m$ ?

*m has 7 possible values*

### 3.78: Orbital

Each valid combination of  $n$ ,  $l$  and  $m$  specifies an orbital.

#### Example 3.79

If  $n = 2$ , what is the number of orbitals?

$$\begin{aligned}l &= 0 \Rightarrow m = 0 \Rightarrow 1 \text{ orbitals} \\l &= 1 \Rightarrow m \in \{-1, 0, 1\} \Rightarrow 3 \text{ orbitals}\end{aligned}$$

$$\text{Total} = 1 + 3 = 4$$

### 3.80: Summary

*n will decide shell*  
*l will decide subshell*  
*m will decide orbital*

### 3.81: Spin

Spin can take two values

$$+\frac{1}{2} \text{ or } -\frac{1}{2}$$

- Spin is not be added or subtracted using arithmetic.
- An orbital cannot have two electrons with same spin.

## B. Electron Configuration

### 3.82: Pauli Exclusion Principle

When filling electrons in shells, no two electrons have same four numbers:

- Principal Quantum Number  $n$
- Angular Momentum Quantum Number  $l$
- Magnetic Quantum Number  $m$
- Spin  $m_s$

#### Example 3.83

What is the number of electrons that can fit in an orbital? What spin do they have?

Two electrons, one with spin  $+\frac{1}{2}$ , and the other with spin  $-\frac{1}{2}$ .

#### Example 3.84

Find the capacity of the  $s$  subshell.

For any value of  $n$  in the  $s$  subshell, we must have:

$$l = 0, m = 0 \Rightarrow (l, m) = (0, 0)$$

We have only one possible pair for  $(l, m)$ .

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

$$(l, m, m_s) = \left(0, 0, -\frac{1}{2}\right) \left(0, 0, +\frac{1}{2}\right) \Rightarrow \text{Capacity} = 2$$

### Example 3.85

Find the capacity of the  $p$  subshells.

For any value of  $n \geq 2$  in the  $p$  subshell, we must have:

$$l = 1, m \in \{-1, 0, 1\} \Rightarrow (l, m) = (1, -1), (1, 0), (1, 1) \Rightarrow 3 \text{ pairs}$$

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

$(l, m, m_s)$  has:

$$3 \times 2 = 6 \text{ values} \Rightarrow \text{Capacity} = 6$$

### Example 3.86

Find the capacity of the  $d$  subshells

For any value of  $n \geq 3$  in the  $p$  subshell, we must have:

$$l = 2, m \in \{-2, -1, 0, 1, 2\} \Rightarrow (l, m) = (2, -2), (2, -1), (2, 0), (2, 1), (2, 2) \Rightarrow 5 \text{ pairs}$$

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

$(l, m, m_s)$  has

$$5 \times 2 = 10 \text{ values} \Rightarrow \text{Capacity} = 10$$

### Example 3.87

Find the capacity of the  $f$  subshells.

For any value of  $n \geq 4$  in the  $p$  subshell, we must have:

$$l = 3, m \in \{-3, -2, -1, 0, 1, 2, 3\} \Rightarrow (l, m) = (3, -3), (3, -2), (3, -1), (3, 0), (3, 1), (3, 2), (3, 3) \Rightarrow 7 \text{ pairs}$$

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

$(l, m, m_s)$  has

$$7 \times 2 = 14 \text{ values} \Rightarrow \text{Capacity} = 14$$

### Example 3.88

Two electrons occupying the same orbital are distinguished by:

42. Two electrons occupying the same orbital are distinguished by
- (a) azimuthal quantum number
  - (b) spin quantum number
  - (c) principal quantum number
  - (d) magnetic quantum number. (NEET-I 2016)

Any orbital has same  $n, l$  and  $m$  values  
The difference will be in

*Spin  $\Rightarrow$  Option B*

### Example 3.89

40. How many electrons can fit in the orbital for which  $n = 3$  and  $l = 1$ ?
- (a) 2
  - (b) 6
  - (c) 10
  - (d) 14 (NEET-II 2016)

$$n = 3, l = 1 \Rightarrow m = \{-1, 0, 1\} \Rightarrow 3 \text{ orbitals}$$
$$\text{Maximum} = 3 \times 2 = 6 \text{ electrons}$$

In other words, it is asking for the capacity of

*$3p \Rightarrow 6 \text{ electrons}$*

## C. Hund's Rule

### 3.90: Hund's Rule

When filling orbitals in a subshell, electrons are unpaired as far as possible.

- Every orbital has a capacity of two electrons, one with positive spin, and the other with negative spin.
- If an electron can occupy an orbital where it is not paired with another electron, it will do that before occupying an orbital where it does get paired.

## D. Sub Level Filling Order



### Aid to Memorizing Sublevel Filling Order

List the sublevels as shown, and read from 1s, following the direction of the arrows. Note that the

- $n$  value is constant horizontally,
- $l$  value is constant vertically, and
- $n + l$  is constant diagonally.



### Example 3.91

Which is the correct order of increasing energy of the listed orbitals in the atom of titanium?

- A.  $4s\ 3s\ 3p\ 3d$
- B.  $3s\ 3p\ 4s\ 3d$

**43.** Which is the correct order of increasing energy of the listed orbitals in the atom of titanium?

(At. no.  $Z = 22$ )

- |                      |                      |        |
|----------------------|----------------------|--------|
| (a) $4s\ 3s\ 3p\ 3d$ | (b) $3s\ 3p\ 3d\ 4s$ |        |
| (c) $3s\ 3p\ 4s\ 3d$ | (d) $3s\ 4s\ 3p\ 3d$ | (2015) |

$3s < 3p < 4s < 3d$   
 Option C

### Example 3.92

- 36.**  $4d$ ,  $5p$ ,  $5f$  and  $6p$  orbitals are arranged in the order of decreasing energy. The correct option is
- (a)  $5f > 6p > 4d > 5p$       (b)  $5f > 6p > 5p > 4d$   
(c)  $6p > 5f > 5p > 4d$       (d)  $6p > 5f > 4d > 5p$   
(NEET 2019)

Option B

## E. Orbital Shapes

### 3.93: s subshell

Every shell has exactly one  $s$  subshell.  
The shape of the  $s$  subshell is spherical.

### 3.94: p subshell

Every shell has exactly three  $p$  subshells:

$p_x$ ,       $p_y$ ,       $p_z$

- $p_x$  orbital lies along the  $x$  axis,
- $p_y$  orbital lies along the  $y$  axis
- $p_z$  orbital lies along the  $z$  axis

$p_x$ ,  $p_y$  and  $p_z$  are mutually perpendicular

### 3.95: Radial Probability Distribution

### 3.96: Number of Nodes

A subshell has  $n - 1$  radial nodes, where  $n$  is the shell number.

$d_{yz}$  lies in the plane determined by the  $y$  axis and the  $z$  axis  
The lobes of  $d_{yz}$  lie between the  $y$  and  $z$  axes

$d_{xz}$  lies in the plane determined by the  $x$  axis and the  $z$  axis  
The lobes of  $d_{xz}$  lie between the  $x$  and the  $z$  axes

$d_{xy}$  lies in the plane determined by the  $x$  axis and the  $y$  axis  
The lobes of  $d_{xy}$  lie between the  $x$  and the  $y$  axes

$d_{(x^2-y^2)}$  lies in the plane determined by  $x$  and  $y$  axes.  
The lobes lie along the axes (not between the axes)

$d_{z^2}$  has two lobes along the z axis and a central donut shaped region in the xy plane.

Probability density

Probability density refers to the probability of finding an electron at x units from the nucleus

Probability distribution

Probability of finding electron in a shell at a distance of x units from the nucleus

13

### Example 3.97

41. Which of the following pairs of  $d$ -orbitals will have electron density along the axes?

(a)  $d_{z^2}, d_{xz}$

(b)  $d_{xz}, d_{yz}$

(c)  $d_{z^2}, d_{x^2 - y^2}$

(d)  $d_{xy}, d_{x^2 - y^2}$

(NEET-II 2016)

Option C

### 3.98: Outer (Valence) and Inner Electrons

- Electrons in the outermost shell are called outer(valence) electrons.
- Remaining electrons are called inner electrons.

## F. Atomic Properties

### 3.99: First In-First Out Rule

## 3.5 Trends in Atomic Properties

### A. Atomic Radius

### 3.100: Trends in Atomic Radius

Atomic radius generally

- increases down a group.
- decreases across a period.

### Example 3.101

	Inner Electrons	$Z$	Outer Electrons
Lithium	2	3	1
Beryllium	2	4	2

1. Lithium and Beryllium have same number of inner electrons. Hence, the shielding provided by the inner electrons in both lithium and beryllium is similar.
  - ✓ This has no effect on atomic radius.
2. Lithium has 1 outer electron. Beryllium has 2 outer electrons. They repel each other, and go further apart.
  - ✓ This has the effect of increasing the atomic radius.
3. Beryllium has  $Z = 4$ , which is greater than  $Z = 3$  for Lithium. Hence, attraction on outer electrons due to the nucleus is greater for Beryllium than for Lithium
  - ✓ This has the effect of decreasing the atomic radius.

The reduction in radius due to point 3 is more than the increase in the radius due to point 2.

Hence, the overall effect is an increase in radius.

## B. Ionization Energy

### 3.102: Ionization Energy

Ionization energy is the energy required for the complete removal of 1 mol of electrons from 1 mol of gaseous atoms or ions.

### 3.103: Reactions

Atoms with a low IE tend to lose their electrons easily, and hence form cations (*+ve ions*) during reactions. Atoms with a high IE tend to not lose their electrons easily, and hence form anions (*-ve ions*) during reactions.

- Exception to atoms with a high IE forming anions are the noble gases.

### Example 3.104

Explain using Coulomb's law why ionization energy usually increases as atomic size decreases.

$$F = k_e \frac{q_1 q_2}{r^2} \Rightarrow F \propto \frac{1}{r^2}$$

As atomic size decreases, the atomic radius decreases, and the force of attraction increases.

## C. Electron Affinity

### 3.105: Ionization Energy

Electron affinity is the energy change accompanying the addition of 1 mol of electrons to 1 mol of gaseous atoms or ions.

## D. Redox Reactions

In a chemical reaction:

1. Oxygen will gain electrons.
2. Oxygen is an oxidizing agent
3. An oxidizing agent oxidizes other elements. In the process, oxygen will get reduced.

In a chemical reaction:

1. Lithium will lose electrons
2. Lithium is a reducing agent
3. Lithium will reduce other elements. In the process, lithium will itself get oxidized.

## E. Acidic versus Basic Nature

Acid + Base = Salt + Water

### 3.106: Down a Group

1. As you go down a group, metallic nature increases.
2. Metals form oxides that act as bases in water.

From Statement I, as you go down a group, the metallic nature will increase. From Statement II, as the metallic nature increases, the tendency to act as a base increases.

For example, the oxide of nitrogen forms a strong acid (nitric acid).  
Going down the group, phosphorus forms a weaker acid ( $\text{H}_3\text{PO}_4$ )

Oxide of arsenic is weakly basic

Bismuth is most metallic and it forms a basic oxide.

## 4. OTHER TOPICS

### 4.1 Chemical Kinetics

#### A. Definition and Theory

##### 4.1: Chemical Kinetics

Chemical kinetics is the study of reaction rates.

##### 4.2: Reaction Rate

Reaction Rate is the change in concentration of reactants (or products) as a function of time.

##### Example 4.3

Fast vs. Slow Rates

##### 4.4: Factors affecting reaction rate

Factors that affect reaction rate are:

- Concentration of reactants
- Physical state of reactants
- Temperature of the reaction
- Presence (or absence) of a catalyst

##### 4.5: Concentration

For a reaction to occur, molecules must collide.

$$\text{Rate} \propto \text{Collision frequency} \propto \text{Concentration}$$

##### 4.6: Physical State

Molecules must mix to collide

If the reactants are in the same phase, they can mix, or can be mixed (externally).

If they are in different phases, contact occurs only at the interface of the phases.

For reactants in different phases, an increase in surface area increases the rate of the reaction substantially.

##### 4.7: Temperature

At higher temperature

- molecules move faster, collisions occur more frequently, and so more molecules react
- energy of collisions increases, and so more molecules react

$$\text{Rate} \propto \text{Collision frequency} \propto \text{Temperature}$$

#### B. Formula

##### 4.8: Rate of reaction

For the reaction  $R \rightarrow P$ , where  $R$  is a reactant and  $P$  is a product:

$$R = - \frac{\Delta(\text{conc } R)}{\Delta t}$$

$$P = \frac{\Delta(\text{conc } P)}{\Delta t}$$

Reactant concentration decreases, so we use negative sign to make it positive:

$$\Delta(\text{conc } R) = \text{conc } R_2 - \text{conc } R_1 < 0$$

Product does not need negative sign since product concentration increases.

$$\Delta(\text{conc } P) = \text{conc } P_2 - \text{conc } P_1 > 0$$

## 4.9: Types of Rates

*Average Rate = Slope*

$$\text{Instantaneous Rate} = \frac{d}{dt}[R]$$

*Initial Rate = Value*

## 4.10: Coefficient of Balanced Chemical Equation

$$aA + bB \rightarrow cC + dD$$
$$\text{Rate} = -\frac{1}{a} \frac{d}{dt}[A] = -\frac{1}{b} \frac{d}{dt}[B] = \frac{1}{c} \frac{d}{dt}[C] = \frac{1}{d} \frac{d}{dt}[D]$$

## C. Rate Law

### 4.11: Rate

For the reaction  $aA + bB \rightarrow cC + dD$

$$\text{Rate} = k[A]^m[B]^n$$

Where

- $k$  = rate constant  $k$  depends on the reaction and the temperature
- $m$  and  $n$  are reaction orders

Rate, reaction orders and rate constant must be found by experiment.

## 4.2 Equilibrium

### A. Basics

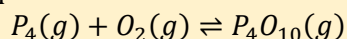
### 4.12: Law of Chemical Equilibrium

For a reaction of the type  $aA + bB \rightleftharpoons cC + dD$ , the equilibrium expression is:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

#### Example 4.13

The quantity of  $P_4$  is one mole, the quantity of  $P_4O_{10}$  is six-tenth of a mole, and the quantity of  $O_2$  is 0.12 of a mole, then find  $K$  using the equilibrium equation

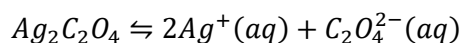


$$K = \frac{[P_4O_{10}]}{[P_4][O_2]} = \frac{0.6}{1 \cdot 0.12} = 5.0$$

## B. Solubility Equilibrium

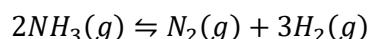
### Example 4.14

Silver oxalate dissolves in water. The concentration of the silver



$$K_{sp} = [Ag^+]^2[C_2O_4^{2-}] = [2.2 \times 10^{-4}]^2[1.1 \times 10^{-4}] = 5.324 \times 10^{-12} \approx 5.3 \times 10^{-12}$$

### Example 4.15

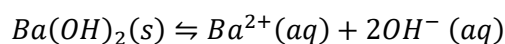


$$K = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

Substitute  $K = 9 \times 10^3$ ,  $NH_3 = 0.03 M$ ,  $H_2 = 0.025 M$

$$9 \times 10^3 = \frac{[N_2][0.025]^3}{[0.03]^2}$$
$$[N_2] = 5.184 \times 10^5 \approx 5 \times 10^5 M$$

### Example 4.16



Convert to moles:

$$1.31 \times 10^{-3} g \times \frac{1 \text{ mol}}{171.34 g} = 7.65 \times 10^{-6} = x$$

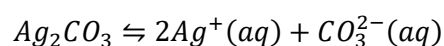
Solubility product constant:

$$K_{sp} = [Ba^{2+}][OH^-]^2 = [x][2x]^2 = x \cdot 4x^2 = 4x^3$$

Substitute  $x = 7.65 \times 10^{-6}$

$$= 4(7.65 \times 10^{-6})^3 \approx 1.79 \times 10^{-15}$$

### Example 4.17

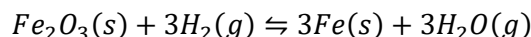


$$K_{sp} = [Ag^+]^2[CO_3^{2-}]$$
$$1.4 \times 10^{-6} = [2x]^2[x]$$
$$1.4 \times 10^{-6} = 4x^2 \cdot x$$
$$1.4 \times 10^{-6} = 4x^3$$



$$\begin{aligned}\text{Carbonate Concentration} &= 2x = 7.0 \times 10^{-3} \text{ M} \\ \text{Silver Concentration} &= 2x = 1.4 \times 10^{-2} \text{ M}\end{aligned}$$

### Example 4.18



$$K = \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3} = \frac{0.37^3}{0.45^3} = 0.56$$

## 4.3 Redox Reactions

### A. Oxidation and Reduction

#### 4.19: Oxidation and Reduction

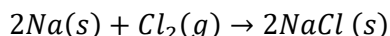
Oxidation is *loss* of electrons.

Reduction is *gain* of electrons.

*Reduction* is *gain*, which is the opposite of what is true in real life.

### Example 4.20

Sodium reacts with chlorine to form sodium chloride. Write the balanced chemical equation for the reaction. Identify oxidation and reduction in this equation.



Sodium:

$\text{Na}^{1+} \Rightarrow$  Sodium loses electrons  $\Rightarrow$  It is oxidized

$\text{Cl}^{1-} \Rightarrow$  Chlorine gains electrons  $\Rightarrow$  It is reduced

#### 4.21: Metal-Non metal reactions

When a metal reacts with a nonmetal to form an ionic compound, electrons are transferred from the metal to the nonmetal. So, in these reactions:

- metal is oxidized (loses electrons)
- nonmetal is reduced (gains electrons)

### B. Oxidation States

#### 4.22: Sanity Check: Electrically Neutral Compounds

For an electrically neutral compound, the sum of the oxidation states must be zero.

#### 4.23: Ionic Compound

In an ionic compound, the charges can be directly identified from the ions.

### Example 4.24

Identify the charges on Sodium Fluoride.

$\text{Na}, +1$



#### 4.25: Uncombined Element

In an uncombined element, the atoms are neutral.

#### Example 4.26

*Chlorine*



#### 4.27: Covalent Compound

In a covalent compound, imaginary charges are assigned based on electronegativity.

#### 4.28: Highly electronegative elements

The most highly electronegative elements are fluorine, oxygen, nitrogen, and chlorine.  
They are assigned oxidation states equal to their charges as an anion.

#### Example 4.29

Assign imaginary charges for ammonia.



We will first assign charge to the nitrogen:

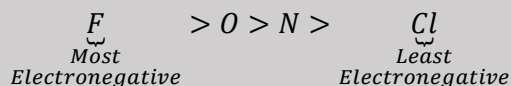


And that gives us:



#### 4.30: Combine Highly electronegative elements

If the highly electronegative elements are together in a compound, we assign charges based on their relative electronegativity.



#### 4.31: Sanity Check: Ionic Species

Sum of the oxidation states must equal the overall charge

#### Example 4.32

Assign imaginary charges for nitrate.



$O$  gets a charge of  $-2 \Rightarrow O_3$  gets  $-6$   
 $N$  needs to balance  $= -6 + 1 = -5 \Rightarrow N = 5$

### 4.33: Hydrogen

In covalent compounds with non-metals, hydrogen has an oxidation state of +1.

### Example 4.34

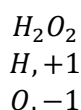
### 4.35: Oxygen

Oxygen has an oxidation state of  $-2$  in covalent compounds.

Exception: peroxides (compounds containing the  $O_2^{2-}$  group), where each oxygen is  $-1$ .

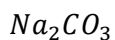
### Example 4.36

Assign imaginary charges for hydrogen peroxide.



### Example 4.37

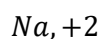
Assign imaginary charges for sodium carbonate.



First assign to oxygen:



Then assign to sodium



And finally:



Charge on  $CO_3^{2-}$  ion is:

$$+4 - 3(2) = 4 - 6 = -2 \Rightarrow \text{Matches}$$

## C. Oxidation States vs. Formal Charge

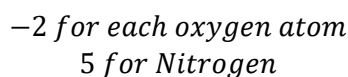
### 4.38: Oxidation States vs. Formal Charge

- Formal charge assumes that shared electrons in a bond are equally shared.
- Oxidation states assume that shared electrons are with the most electronegative atom.

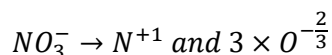
### Example 4.39

Compare oxidation states and formal charge for the nitrate ion.

Oxidation State



Formal Charge

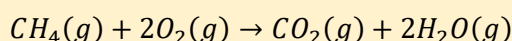


## D. Oxidizing and Reducing Agents

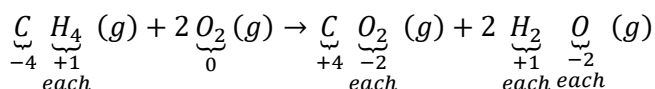
### 4.40: Oxidizing and Reducing Agents

In a chemical reaction, we can the change in the oxidation states to identify oxidizing and reducing agents.

#### Example 4.41



- The combustion reaction for methane yields carbon dioxide and water vapor. Write a balanced chemical reaction.
- What is being oxidized, and what is being reduced
- Identify oxidizing and reducing agents



Carbon

Oxidation State:  $-4$  to  $+4$   
 8e lost  
 Oxidized  
 CH<sub>4</sub>: Reducing Agent

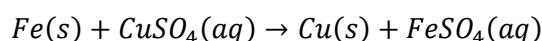
Oxygen

Oxidation State:  $0$  to  $-2$   
 8e gained  
 Reduced  
 O<sub>2</sub>: Oxidizing Agent

#### Example 4.42

If an iron nail is immersed in copper sulphate solution, the iron displaces the copper.

- Write a balanced chemical reaction.
- What is being oxidized, and what is being reduced
- Identify oxidizing and reducing agents



Copper

$+2$  to  $0$   
 Reduced  
 Oxidizing Agent

Iron

$0$  to  $+2$   
 Oxidized  
 Reducing Agent

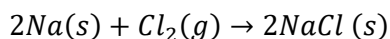
Sulphate

$-2$  to  $-2$   
*Unchanged*

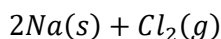
## E. Balancing using Half-Reactions

### 4.43: Breaking a Reaction

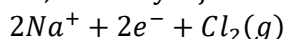
The reaction between sodium and chlorine to form sodium chloride is:



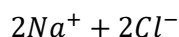
Begin with the reactants:



In the reaction, two electrons from the sodium get transferred to the chlorine. In a thought experiment, imagine a state where the electrons have left the sodium, but not yet joined the chlorine:



Then the electrons join the chlorine:

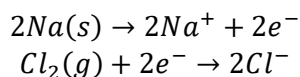


And we know that the formula unit for the sodium chloride compound is  $\text{NaCl}$ :

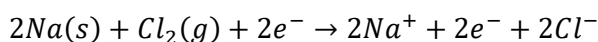


### 4.44: Half Reactions

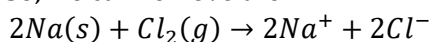
We can break a reaction into two half reactions.



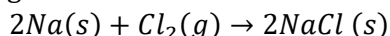
Add the two reactions:



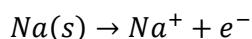
There are two electrons on both sides. So, we can remove them:



And we can write the sodium chloride together:



### Example 4.45

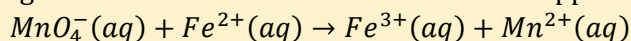


### 4.46: Acidic versus Basic Medium

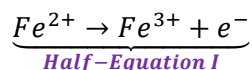
Reactions can happen in either an acidic or a basic medium.

### Example 4.47

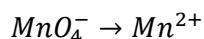
Balance the reaction below using the half reaction method. The reaction happens in an acidic medium:



Start with the iron:



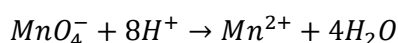
The second half of the equation:



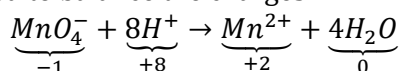
The oxygen on the reactant side is missing on the product side. Balance the oxygen by adding water:



Adding the water balances the oxygen, but adds hydrogen on the product side. Balance the hydrogen by adding  $\text{H}^+$  on the reactant side:

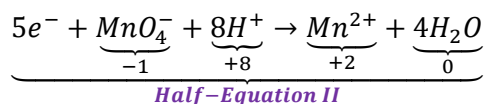


Now, the elements are balanced. We need to balance the charges.

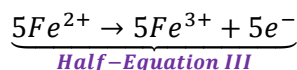


$$\text{Net Reactant Charge} = -1 + 8 = 7$$

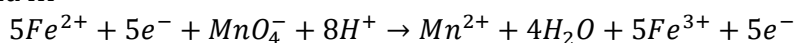
$$\text{Net Product Charge} = -1 + 8 = 2$$



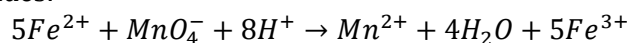
Multiply half-equation I by 5:



Add half-equations II and III



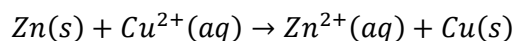
Cancel the electrons on both sides:



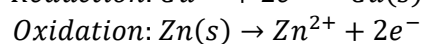
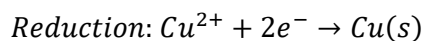
## 4.4 Electrochemistry

### A. Daniel Cell

#### 4.48: Daniel Cell



This can be split into two half reactions:



#### 4.49: Cathode and Anode

Anode:

- Oxidation takes place at anode.
- By convention, in diagram, anode on the left

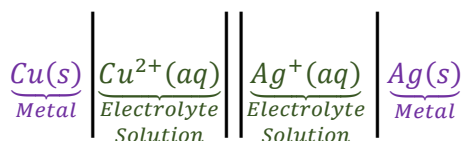
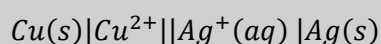
Cathode

- Reduction takes place at cathode.
- By convention, in diagram, cathode on the right

#### 4.50: Current Flow

Direction of current flow is opposite to direction of electron flow.

#### 4.51: Cell Representation



#### 4.52: Cell Potential

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

- Cell potential is the potential difference between the two electrodes of a galvanic cell.
- When there is no current, cell potential is the same as cell emf (electromotive force).

#### Example 4.53

The cell potential for the cell  $\text{Cu(s)}|\text{Cu}^{2+}||\text{Ag}^+(\text{aq})|\text{Ag(s)}$  is

$$E_{\text{cell}} = E_{|\text{Ag}^+(\text{aq})|\text{Ag(s)}} - E_{|\text{Cu(s)}|\text{Cu}^{2+}|}$$

#### 4.54: Hydrogen as Benchmark / Zero Potential Cell

Potential of half-cell cannot be measured individually.

Consider hydrogen as zero potential

#### 4.55: Standard electrode potential

$$E^\theta = E_R^\theta$$

$$E^\theta = E_R^\theta - E_L^\theta$$

Using zero potential cell on left:

$$E^\theta = E_R^\theta - 0 = E_R^\theta$$

#### 4.56: Interpreting standard electrode potential

- Positive value of  $X$  means hydrogen can reduce  $X$
- Negative value of  $X$  means hydrogen can oxidize  $X$ .

Where  $X$  is element.

### Example 4.57

Interpret:

- A.  $Pt(s) | H_2(g, 1 \text{ bar}) | H^+(aq, 1 M) || Cu^{2+}(aq, 1 M) | Cu$  has standard electrode potential  $0.34V$
- B.  $Pt(s) | H_2(g, 1 \text{ bar}) | H^+(aq, 1 M) || Zn^{2+}(aq, 1 M) | Zn$  has standard electrode potential  $-0.76V$

$0.34 V$

Hydrogen can reduce copper

$-0.76V$

Hydrogen can oxidize zinc

## 4.5 Further Topics

### 58 Examples