

Zagazig University
Faculty of Science
Chemistry Department



Chemistry 101

Physical Chemistry (1)

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Chemistry 101

Physical Chemistry (1)

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General Chemistry

Gaseous State

All matter exists in three states: gas, liquid and solid. A molecular level representation of gaseous, liquid and solid states is shown in Figure (1).

A gas consists of molecules separated wide apart in empty space. The molecules are free to move about throughout the container.

A liquid has molecules touching each other. However, the intermolecular space, permit the movement of molecules throughout the liquid.

A solid has molecules, atoms or ions arranged in a certain order in fixed positions in the crystal lattice. The particles in a solid are not free to move about but vibrate in their fixed positions.

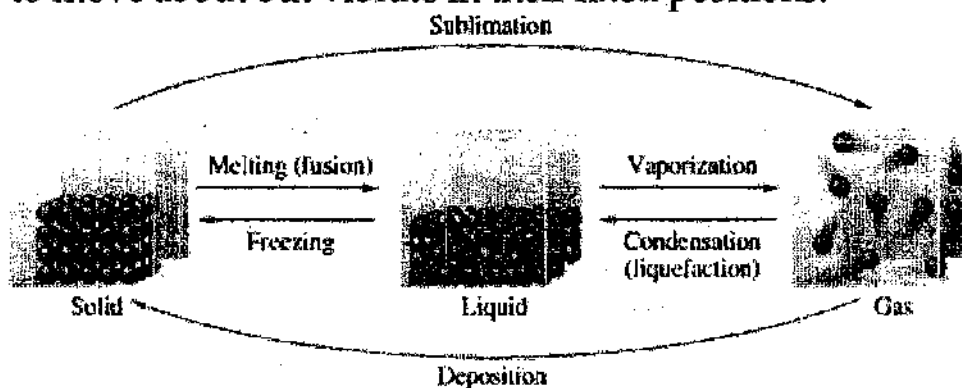
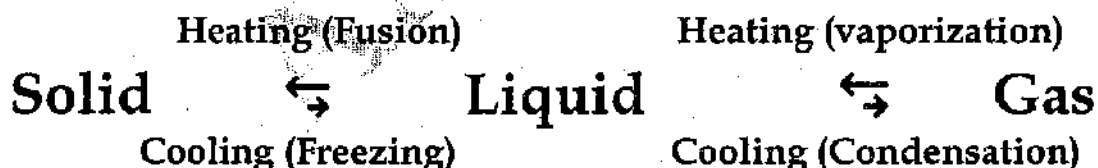


Figure (1) The material changes from state to another state



GENERAL CHARACTERISTICS OF GASES

1. **Expansibility:** Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.
2. **Compressibility:** Gases are easily compressed by application of pressure to a movable piston fitted in the container.
3. **Diffusibility:** Gases can diffuse rapidly through each other to form a homogeneous mixture.
4. **Pressure:** Gases exert pressure on the walls of the container in all directions.

5. **Effect of Heat:** When a gas, confined in a vessel is heated, its pressure increases. Upon heating in a vessel fitted with a piston, volume of the gas increases.

The above properties of gases can be easily explained by the Kinetic Molecular Theory which will be considered later in the chapter.

The material is not discontinuance for specific state but may whatever one of three states according to the surrounding circumstances. Therefore it must be define the circumstances and and condidions, as example the standard or normal condition (STP), i.e., standard pressure and temperature, which means that the pressure is equal to one atmosphere (1.0 atm) and temperature is equal to zero centigrade (0.0°C). Also, it was an agreement that the 25°C is taken as room temperature in the entire world regardless of the real temperature.

General Physical Properties of Gases

The gases are characterized by some properties tan the other material states. The gas molecules exist at separet distances and according to that the attractive forces between gas molecules are so weak. These weak attractive forces permit to continuous, fast, eternal and random movement of gas particles.

All gases are capable for mixing to each others with any ratio to form a solution, which is argued to the intermediate distances between the gas molecules where the gas molecules interpenetrate between that intermediate distanes for another gas. It follows this gas can be compressed to less volume and lowering the intermediate distanes and adjacent the gas molecules to each others. The low densities of gases give the gases the ability of diffusion and occupy the total vessel volume. The gas density can be reduced or increased by changing the gas quantity or the occupied volume by controlling the pressure or temperature of both of them.

It is clear that gas properties closely related to four variables:

Pressure (P), Volume (V), Temperature (T) and Quantity (n)

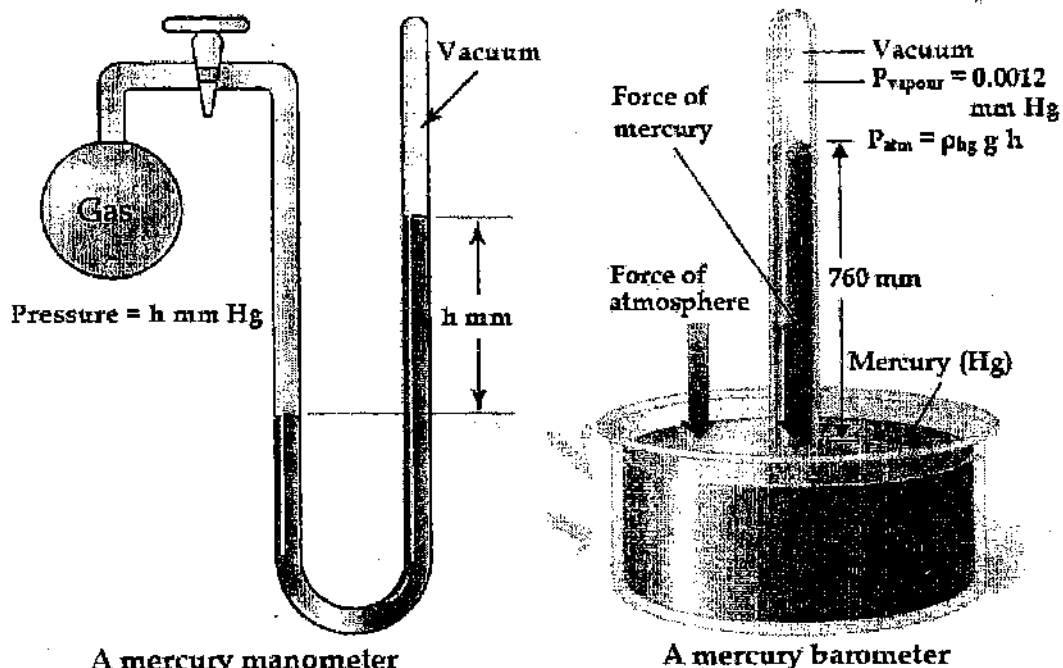
The Pressure (P): is defined as the effective force to the unit area.

The gas pressure is a result of the collsion strength of its particle with to the area walles of the conainting vessel

$$\text{Pressures unite} = \frac{\text{force}}{\text{area}}$$

$$P \text{ (unit)} = \frac{\text{kg m s}^{-2}}{\text{m}^2} = \text{kg m}^{-1} \text{ s}^{-2} = \text{Pascal (Pa)}$$

The pascal is unit of the international world units. It is defined as the strength which equivalent to one Neuton ($1.0 \text{ N} = 1.0 \text{ kg m s}^{-2}$) and effective to one square meter area (1.0 m^2). The gas pressure can be measured using a mercury manometer or barometer as in Figure (2).



A mercury manometer

A mercury barometer

Figure (2) A Mercury Manometer and A Mercury Barometer

A mercury barometer is a long glass tube ($80 \times 1 \text{ cm}$), which is filled with mercury, and then inverted into a reservoir of mercury. The mercury in the tube immediately seeks a height so that the pressure exerted on the surface of the mercury in the reservoir is exactly balanced by the pressure exerted by the mercury column. The height of the mercury column that will be balanced by a pressure of exactly 1 atmosphere is 760 millimeters (mm Hg) at sea level.

A simple manometer can be made using a U-shaped glass tube filled with mercury. One end of the tube opens into the container in which the gas pressure is to be measured. The other end of the tube is open to the surrounding atmosphere. To determine the pressure in the container, calculate the difference between atmospheric pressure and the pressure in the container (the difference between the heights of the two mercury columns).

The pressure of the earth is a mixture of gases which exert pressure is called the atmospheric pressure, it is the compressive force at earth surface or the weight of atmosphere divided to the earth area under this weight, or the weight (Neuton) the weight of coloumn of air it cross section 1 m^2 . But there is differentiation between the sea bottom, valleys bottom and deep grooves than the top of high mountains. The weight in deep vally is more than the weight ate sea level which is also more than that in the top of High Mountain as shown in Figure (3). According to this the atmosphere will be different and the quantity of air will be more at low temperature and less at higher temperature. Therefore, for these two resons, come in terms the the atmosphere quantity at sea level and at temperature 0.0°C is known as the standard pressure which is equal to:

$$\text{Standard Pressure} = 101325 \text{ Pa} = 1 \text{ atm}$$

i.e., 1.0 atmosphere (1 atm) is the weight (Neuton) the air coloumn of cross section 1m^2 at sea level and temperature 0.0°C .

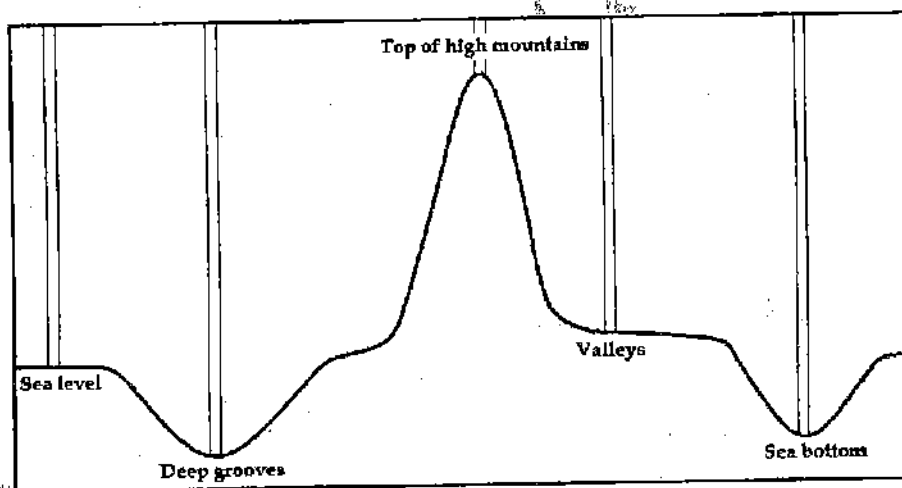
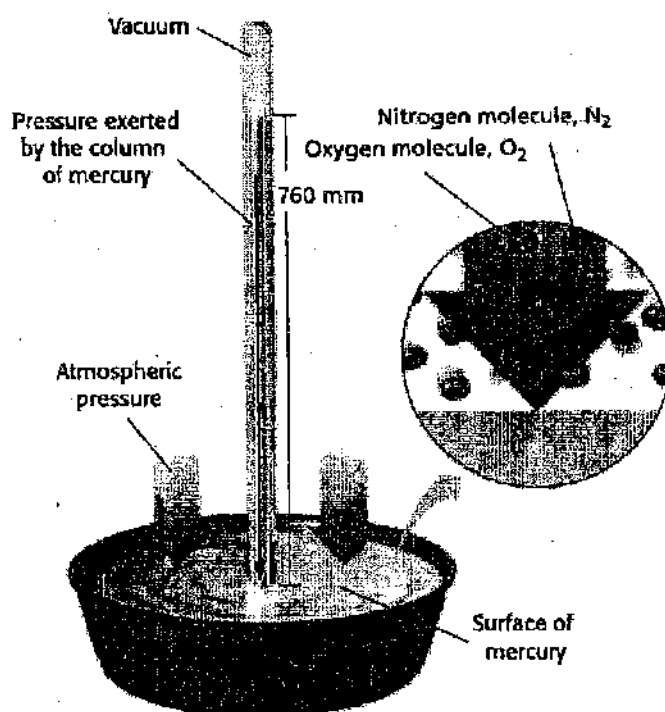


Figure (3) The differentiation of atmosphere with different places.

Measurement of the Atmosphere:

Torrceilli could measure the atmosphere with his inventiveness to the barometer, which is consisted of glass tube with one meter length and closed from one side and evacuated and filled with mercury, then turned over in tank of mercury; it was found that the hight of mercury in the tube is definit at definit temperature. This mercury length can not be stilled without the pressure of the atmosphere pressure on the mercury in the tank. It was founded that the mercury length

Measurement of atmosphere: The weight (Neuton) coulumn of air with cross section 1 m². Torrcelli could to measure the atmosphere pressure with his invention to the baromter, which is consists of a evacuated glass tube with 1m length and closed from one side anf is filled with mercury, then turned over in a tank filled also with mercury. It is noticed that the mercury column in the glass tube takes a definite hight. This hight is not possible to stay existing in the glass tube as a result of atmosphere pressure at the mercury surface in the tank to bracer the mercury column to be in definit hight.



In the sealed column of a barometer, the mercury falls until the pressure exerted by its weight equals the atmospheric pressure

$$P_{\text{atm}} = \rho_{\text{Hg}} \cdot g \cdot h$$

$$P_{\text{atm}} = (13595 \text{ kg/cm}^3) (9.807 \text{ m/s}^2) (0.760 \text{ m})$$

$$P_{\text{atm}} = 101325 \text{ Pa} = 17696 \text{ lb/in}^2$$

It was found that the mercury length at sea level and temperature 0.0°C is equal to 76 cm (760 mm), which leads to take this as atmosphere pressure unite.

$$1 \text{ atm} = 76 \text{ cm Hg} = 760 \text{ mm Hg} = 760 \text{ torr}$$

$$1 \text{ atm} = 101325 \text{ Pa} = 101.325 \text{ kPa}$$

Honoring to *Torrceili* the baromter inventor, 1.0 mmHg = 1 torr

The volume of a given sample of gas depends on the temperature and pressure applied to it. Any change in temperature or pressure

will affect the volume of the gas. As results of experimental studies from 17th to 19th century, scientists derived the relationships among the pressure, temperature and volume of a given mass of gas. These relationships, which describe the general behaviour of gases, are called the gas laws.

Pressure Conversion Factors:						
unit	Pa	kPa	bar	atm	torr	psi
1 Pa	1	10^{-3}	10^{-5}	9.86923×10^{-6}	7.50062×10^{-3}	1.45038×10^{-4}
1 kPa	10^3	1	10^{-2}	9.86923×10^{-3}	7.50062	0.145038
1 bar	10^5	10^2	1	0.986923	750.062	145.038
1 atm	101325	101.325	1.01325	1	760	14.6959
1 torr	133.322	0.133322	1.33322×10^{-3}	1.31579×10^{-3}	1	1.93367×10^{-2}
1 psi	6894.76	6.89476	6.89476×10^{-2}	6.80460×10^{-2}	51.71507	1
a.	Pascal	kiloPascal	bar	atmosphere	torr	pound per square-inch

(1) Boyle's Law

In 1660 Robert Boyle found out experimentally the change in volume of a given sample of gas with pressure at room temperature. From his observations he formulated a generalisation known as Boyle's Law. It states that: "At constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure". If the pressure is doubled, the volume is halved

$$P \propto \frac{1}{V} \Rightarrow P \propto \frac{K_1}{V}$$

$$PV = K_1$$

$$\therefore P_1V_1 = P_2V_2 = P_3V_3 = K_1 = \text{constant}$$

Example 1: The value of pressure of quantity of a gas in container vessel its volume is "4L" is 2.0 atm at temperature 0.0°C. How much will be the pressure of the same quantity of gas at the same temperature if the volume is changed to "2L"?

∴ The gas quantity and temperature are constant.

∴ According to Boyle's law: $P_1V_1 = P_2V_2$

$$P_1 = P_2 \times \frac{V_1}{V_2} = 2 \text{ atm} \times \frac{4 \text{ L}}{2 \text{ L}} = 4 \text{ atm}$$

(2) Charles Law and Gay Lussac's Law

In 1787 Jacques Charles investigated the effect of change of temperature on the volume of a fixed amount of gas at constant pressure. He established a generalisation which is called the Charles' Law. It states that: at constant pressure, the volume of a fixed mass of gas is directly proportional to the Kelvin temperature of absolute temperature. If the absolute temperature is doubled, the volume is doubled.

The Scientist Gay Lusac has put the following law which has been also obtained before by Charle in 1787, which illustrates the relation between the gas volume and its temperature at constant pressure and quantity.

"At constant pressure the volume of a quantity of gas increases (or decreases) by $\frac{1}{273}$ of its volume at the absolute temperature if the gas temperature increases (or decreases) by one centigrade".

i.e., the gas volume at temperature -273°C is zero, i.e., the gas is vanished at this temperature, which definitely conflicts with law of material. From the experimental side, as lowering the gas temperature till very low temperature but more than -273°C , the gas will be changed to liquid, and Charles and Gay Lusac law will be not applicable any more because it not be a gas anymore also. But, it is possible to imagine this case theoritially as shown in Figure (7).

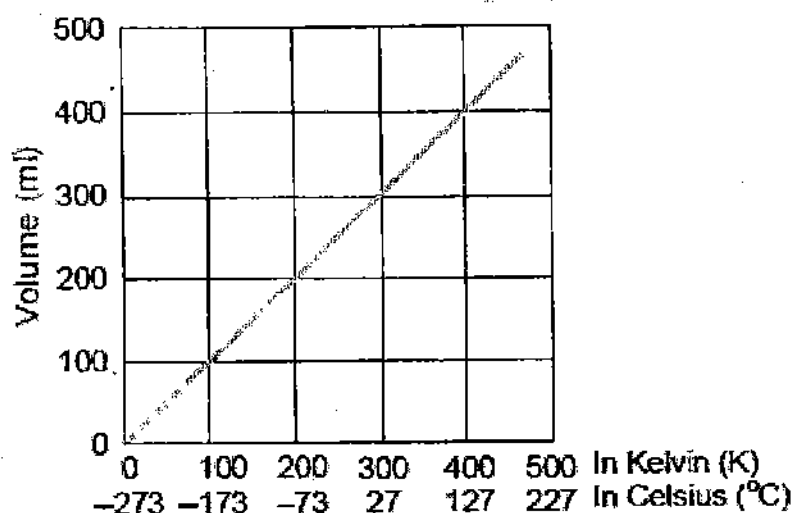


Figure (7) Graph showing that at constant pressure, volume of a given mass of gas is directly proportional to the Kelvin temperature

Lord Kelvin considered the degree of temperature -273°C as base to new temperature graduation and called it as absolute temperature, at which the volume reaches the zero value. It takes the symbole K.

$$0.0 \text{ K} = 273^{\circ}\text{C} \quad \Rightarrow \quad 273^{\circ}\text{C} = 0.0 \text{ K}$$

$$0.0 \text{ K} = t^{\circ}\text{C} + 273 \quad \Rightarrow \quad t^{\circ}\text{C} = (273 + t) \text{ K}$$

Whereas "T" is the absolute temperature, the relation between them and the cellius temperature "t" is as the following equation (1):

$$V = \frac{V_0}{273} \cdot T \quad \Rightarrow \quad V = \frac{V_0}{273} (273 + t)$$

where V_0 = gas volume at 0.0°C = constant.

$$\frac{V}{T} = K_2 \quad \Rightarrow \quad V = K_2 T$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \dots\dots\dots = K_2 = \text{constant}$$

Therefore, the Charles and Gay Lusac law can be simply paraphrased as follows:

"At constant pressure, the volume of a fixed mass of gas is directly proportional to the Kelvin temperature of absolute temperature"

Example 2: A certain quantity of gas has a volume 22.4 L at pressure 1.0 atm and temperature 0.0°C , what is the volume of the same quantity of a gas at the pressure and room temperature?

$\therefore$ The gas quantity and pressure are constant.

$\therefore$ According to Charle and Gay Lusac Law: $\frac{V_2}{V_1} = \frac{T_2}{T_1}$

$$T_1 = 0.0 + 273 = 273 \text{ K} \quad \& \quad T_2 = 25 + 273 = 298 \text{ K}$$

$$V_1 = 22.4 \text{ L} \quad \& \quad V_2 = ?$$

$$\therefore V_2 = V_1 \times \frac{T_2}{T_1} = 22.4 \text{ L} \times \frac{298 \text{ K}}{273 \text{ K}} = 2.445 \text{ L}$$

(3) Amonton's Law

Amonton could deduced relation between the gas pressure and its temperature as following: **"At constant volume the gas pressure of quantity of gas is directly proportional to its absolute temperature"**.

$$P \propto T \quad \Rightarrow \quad P = K_3 T$$

$$\frac{P}{T} = K_2 \quad \Rightarrow \quad \frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = K_3 = \text{constant}$$

Example 3: A certain quantity of gas is put in container vessel at temperature 30°C under pressure 2.0 atm. How much will be the gas pressure at temperature 0.0°C .

$\therefore$ The gas quantity and volume are constant.

$\therefore$ According to Amonton Law: $\frac{P_2}{P_1} = \frac{T_2}{T_1}$

$$T_1 = 30 + 273 = 303 \text{ K} \quad \& \quad T_2 = 0.0 + 273 = 273 \text{ K}$$

$$P_1 = 2.0 \text{ atm} \quad \& \quad P_2 = ?$$

$$P_2 = P_1 \times \frac{T_2}{T_1} = 2 \text{ atm} \times \frac{273 \text{ K}}{303 \text{ K}} = 1.8 \text{ atm}$$

(4) Avogadro's Law

Suppose we have a ballon containing a quantity of gas, by addition another quantity of a gas and controlling the absolute temperature

(T) and pressure (P) constant internal the ballon. It is noticed that the ballon volume is increased, i.e., as the number of moles (n) of the gas increased the gas volume (V) increased at constant temperature and pressure which means that:

$$V \propto n \quad \Rightarrow \quad V = K_4 n$$

$$\frac{V}{n} = K_4 \quad \Rightarrow \quad \frac{V_1}{n_1} = \frac{V_2}{n_2} = \frac{V_3}{n_3} = K_4 = \text{constant}$$

In case of equality of the volumes at the same conditions of pressure and temperature:

$$\therefore V_1 = V_2 \quad \Rightarrow \quad \therefore n_1 = n_2$$

Which means that for two equal volumes of two different gases at constant pressure and temperature, the numbers of moles for both gases are equal. This is the principle of Avogadro's Law:

"At the same condition of pressure and temperature, the equal volumes of gases contains the same number of molecules".

The Molar Volume:

At constant T and P, whereas $K_4 = \frac{V}{n}$, i.e., the volume of a certain quantity (n) from any gas is constant at constant pressure and temperature. When this quantity is one mole only, its volume is called the **molar volume** and symbolized by V_m , i.e. the molar volume of any gas at standard conditions (STP) is equal to 22.4 liter.

Example 4: The volume of one mole of a gas at definite pressure and temperature is 10 L. What is the volume of 5 moles from that gas at the same conditions?

∴ The gas pressure and temperature are constant.

∴ According to Avogadro's Law: $\frac{V_2}{V_1} = \frac{n_2}{n_1}$

$$\begin{array}{ccc} V_1 = 10 \text{ L} & \& V_2 = ? \\ n_1 = 1 \text{ mol} & \& n_2 = 5 \text{ mol} \end{array}$$

$$\therefore V_2 = V_1 \times \frac{n_2}{n_1} = 10 \text{ L} \times \frac{5 \text{ mol}}{1 \text{ mol}} = 50 \text{ L}$$

5) P - n Relationship

"At constant volume and temperature, the gas pressure is directly proportional to its quantity".

$$P \propto n \quad \Rightarrow \quad P = K_5 n$$

$$\frac{P}{n} = K_5 \quad \Rightarrow \quad \frac{P_1}{n_1} = \frac{P_2}{n_2} = \frac{P_3}{n_3} = K_5 = \text{constant}$$

Example 5: At certain temperature, an oxygen cylinder contains 15 kg under pressure 28 atm, what will be its pressure at the same temperature after its half quantity is consumed?

∵ The gas volume is constant (cylinder volume) and temperature is constant.

∴ According to the relation between the gas pressure and its quantity at constant (V & T):

$$\begin{aligned} \frac{P_2}{P_1} &= \frac{n_2}{n_1} \\ P_1 &= 28 \text{ atm} & \& & P_2 &=? \\ n_1 &= n \text{ mol} & \& & n_2 &= \frac{1}{2}n \text{ mol} \\ \frac{P_2}{P_1} &= \frac{n_2}{n_1} & \& & \frac{n_2}{n_1} &= \frac{\frac{1}{2}n}{n} = 0.5 \\ \therefore P_2 &= P_1 \times \frac{n_2}{n_1} = 28 \text{ atm} \times 0.5 = 14 \text{ atm} \end{aligned}$$

5) n - T Relationship

The text relation: "At constant pressure and volume, the gas quantity is inversely proportional to its absolute temperature".

$$n \propto \frac{1}{T} \quad \Rightarrow \quad n = \frac{K_6}{T}$$

$$n_1 T_1 = n_2 T_2 \dots\dots\dots = k_6 = \text{constant}$$

Example 6: A gas cylinder contains 20 kg of nitrogen under constant pressure at certain temperature. How much the temperature will be after its half quantity is consumed?

∵ The gas volume is constant (cylinder volume) and pressure is constant also (V & P are constants).

∴ According to the relation between the gas quantity and its temperature:

$$\begin{aligned} n_1 T_1 &= n_2 T_2 \\ \frac{n_2}{n_1} &= \frac{1}{2} \quad \Rightarrow \quad \frac{n_1}{n_2} = 2 \\ n_1 T_1 &= n_2 T_2 \\ \therefore T_2 &= T_1 \times \frac{n_1}{n_2} = T_1 \times \frac{2 \text{ mol}}{1 \text{ mol}} = 2 T_1 \end{aligned}$$

State Equation of Gases:

This equation describes the case of certain quantity of gas with the sense of its volume, pressure and temperature. Sometimes is called the unified law of gases or the general relation of gases.

Suppose the presence of certain quantity of gas at constant temperature T_1 .

At pressure P_1 The volume is V_1
At pressure P_2 The volume is V

∴ Temperature and gas quantity are constants (T & n)

∴ according to Boyle's Law: $P_1 V_1 = P_2 V_2$

$$\therefore V = \frac{P_1 V_1}{P_2} \quad (1)$$

If the gas pressure is fixed at pressure P_2

At temperature T_1 The volume is V

At temperature T_2 The volume is V_2

∴ Pressure and gas quantity are constants (T & n)

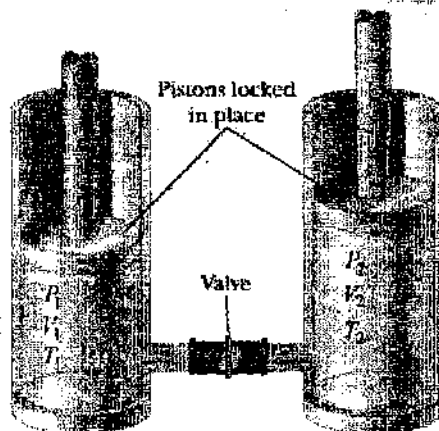
∴ According to Charles and Gay Lussac's law: $\frac{V}{T_1} = \frac{V_2}{T_2}$

$$\therefore V = \frac{T_1 V_2}{T_2} \quad (2)$$

From equation (1) and (2), we can deduce the following:

$$\frac{P_1 V_1}{P_2} = \frac{T_1 V_2}{T_2} \quad (3)$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (4)$$



Example 7: What is the volume of gas at STP, if it occupies a volume 250 cm^3 at room temperature under pressure 85 kPa ?

STP means that:

∴ The quantity (n) is constant.

$$T_1 = 0.0 + 273 = 273 \text{ K}$$

$$P_1 = 101.325 \text{ kPa}$$

$$V_1 = ?$$

$$\& \quad T_2 = 25 + 273 = 298 \text{ K}$$

$$\& \quad P_2 = 85 \text{ kPa}$$

$$\& \quad V_2 = 250 \text{ cm}^3$$

∴ According to state equation:

$$V_1 = V_2 \times \frac{P_2 T_1}{P_1 T_2} = 250 \text{ cm}^3 \times \frac{85 \text{ kPa} \times 273 \text{ K}}{101.325 \text{ kPa} \times 298 \text{ K}} = 192 \text{ cm}^3$$

The Universal Gas Constant (R) and its Value:

Previously, we know :

$$T \propto \frac{1}{n} \quad \& \quad P \propto n \quad \& \quad V \propto n$$

$$\frac{PV}{T} \propto n \quad \Rightarrow \quad \therefore \frac{PV}{nT} = \text{constant} = R$$

The Values of the Constant (R): 1.0 mol of gas occupies 22.4 L at STP, i.e., pressure is equal to 1.0 atm and temperature 273 K.

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}} = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$1.0 \text{ L} = 10^{-3} \text{ m}^3 \quad \& \quad 1 \text{ atm} = 101325 \text{ Pa}$$

$$R = \frac{101325 \text{ Pa} \times 22.4 \times 10^{-3} \text{ m}^3}{1 \text{ mol} \times 273 \text{ K}} = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

$$1.0 \text{ Pa} = 1.0 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$R = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1}$$

$$1 \text{ atm} = 1.013 \times 10^6 \text{ dyne cm}^{-2}$$

$$R = \frac{1.013 \times 10^6 \text{ dyne} \times 22.4 \times 10^3 \text{ cm}^3}{1 \text{ mol} \times 273 \text{ K}} = 8.314 \text{ dyne cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ dyne} = 1 \text{ g cm s}^{-2}$$

$$R = 8.314 \text{ g cm}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ dyne cm} = 1 \text{ erg}$$

$$R = 8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ cal} = 4.184 \times 10^7 \text{ erg}$$

$$R = \frac{8.314 \times 10^7 \text{ erg} \times 1.0 \text{ cal}}{4.184 \times 10^7 \text{ erg} \times \text{mol} \times \text{K}} = 1.988 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$R \approx 2 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ cal} = 4.184 \text{ Joule}$$

$$R = \frac{1.988 \text{ cal} \times 4.184 \text{ J}}{1 \text{ cal} \times \text{mol} \times \text{K}} = 4.184 \text{ J mol}^{-1} \text{ K}^{-1}$$

Table (3) summarize the values and units of gas constant (R)	
0.0821 atm L mol ⁻¹ K ⁻¹	8.314 Pa m ³ mol ⁻¹ K ⁻¹
8.314 kg m ² s ⁻² K ⁻¹	8.314 dyne cm mol ⁻¹ K ⁻¹
8.314 g cm ² s ⁻² mol ⁻¹ K ⁻¹	8.314 erg mol ⁻¹ K ⁻¹
8.314 J mol ⁻¹ K ⁻¹	1.997 cal mol ⁻¹ K ⁻¹

Example 10: Calculate the volume of ammonia gas (NH₃) its weight is 6.85 g at temperature 24°C under pressure 750 mm Hg.

The molecular weight of ammonia gas = 17 g mol⁻¹

$$PV = nRT$$

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

$$V = \frac{wRT}{PM} = \frac{6.5 \text{ g} \times 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 297 \text{ K}}{0.987 \text{ atm} \times 17 \text{ g mol}^{-1}} = 9.944 \text{ L}$$

Example 11: Find the number of moles for carbon monoxide gas $\text{CO}_{(g)}$ in 500 ml container at temperature 50°C under pressure 1.5 atm. Calculate the gas mass ?

The molecular weight of carbon monoxide (CO) = 28 g mol^{-1}

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

$$n = \frac{1.5 \text{ atm} \times 0.5 \text{ L}}{0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 323 \text{ K}} = 0.028 \text{ mol}$$

$$n = \frac{w}{M}$$

$$w = n M = 0.028 \text{ mol} \times 28 \text{ g mol}^{-1} = 0.784 \text{ g}$$

Example 12: What is the volume of 10 g of carbon dioxide gas $\text{CO}_{2(g)}$ at temperature 27°C and pressure 2.0 atm.

The molecular weight of carbon dioxide (CO_2) = 44 g mol^{-1}

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

$$V = \frac{w RT}{P M} = \frac{10 \text{ g} \times 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2 \text{ atm} \times 44 \text{ g mol}^{-1}} = 2.792 \text{ L}$$

Example 13: Dry gas compound, its volume 120 cm^3 at temperature 22°C and pressure 742 mmHg and its weight is 0.82 g. Calculate its molecular weight.

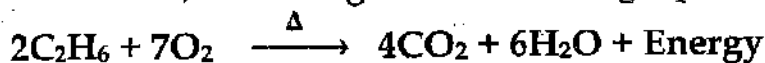
$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{0.97 \text{ atm} \times 0.12 \text{ L}}{0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 295 \text{ K}} = 4.842 \times 10^{-3} \text{ mol}$$

$$n = \frac{w}{M} \quad \Rightarrow \quad M = \frac{w}{n}$$

$$M = \frac{w}{n} = \frac{0.82 \text{ g}}{4.842 \times 10^{-3} \text{ mol}} = 169 \text{ g mol}^{-1}$$

Example 14: Calculate oxygen volume which is necessary for oxidation of 45 g of ethane gas (C_2H_6) at temperature 127°C and under pressure 3 atm, according to the following equation:



The molecular weight of ethane = 30 g mol^{-1}

The number of moles of ethane (n) = $\frac{w}{M} = \frac{45 \text{ g}}{30 \text{ g mol}^{-1}} = 1.5 \text{ mol}$

$$\begin{array}{rcl} 2.0 \text{ mol of } \text{C}_2\text{H}_6 & = & 7.0 \text{ mol O}_2 \\ 1.5 \text{ mol of } \text{C}_2\text{H}_6 & = & x \text{ mol O}_2 \end{array}$$

$$n_{\text{O}_2} = \frac{7 \text{ mol} \times 1.5 \text{ mol}}{2 \text{ mol}} = 5.25 \text{ mol}$$

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{5.25 \text{ mol} \times 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 400 \text{ K}}{3 \text{ atm}} = 57.4 \text{ L}$$

Gas Density and Molar Mass

Material density is defined as the mass of a certain volume at certain temperature, or the weight of unite volume at certain temperature. As a result of the higher influence of temperature on the gas volume than its influence of liquid and solid volumes, it can be recourse of the universal law of gases at different conditions as following:

$$PV = nRT \quad \& \quad n = \frac{w}{M}$$

$$\therefore PV = \frac{w}{M} RT \quad (1)$$

By arrangement equation (1), we get:

$$PM = \frac{w}{V} RT \quad \& \quad d = \frac{w}{V}$$

Whereas d is gas density:

$$\therefore PM = d RT$$

$$d = \frac{MP}{RT} \quad (2)$$

$$\text{The densities unite} = \frac{\text{mass unite}}{\text{volume unite}}$$

$$\therefore d_{\text{unit}} = \frac{w}{V} = \frac{g}{\text{cm}^3} = g/\text{cm}^3 \text{ or } g/L$$

To know its unites, from equation (2):

$$d = \frac{MP}{RT} = \frac{g \text{ mol}^{-1} \times \text{atm}}{\text{L atm mol}^{-1} \text{ K}^{-1} \times K} = g \text{ L}^{-1}$$

Example 25: What is the density of methane gas (CH_4) at STP?

The molecular weight of methane = 16 g mol^{-1}

$$d_{\text{CH}_4} = \frac{MP}{RT} = \frac{16 \text{ g mol}^{-1} \times 1 \text{ atm}}{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}} = 0.715 \text{ g L}^{-1}$$

Example 26: The density of a gas is $2.16 \times 10^{-3} \text{ g cm}^{-3}$ at temperature 100°C and under pressure 1.5 atm . Find the gas molecular weight.

$$d = \frac{2.16 \times 10^{-3} \text{ g cm}^{-3} \times 10^3 \text{ cm}^3}{\text{cm}^3 \times 1 \text{ L}} = 2.16 \text{ g L}^{-1}$$

$$PM = dRT$$

$$M = \frac{dRT}{P} = \frac{2.16 \text{ g L}^{-1} \times 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1.5 \text{ atm}} = 44 \text{ g mol}^{-1}$$

Amagat Law for Partial Volumes

The molar volume of any gas in a mixture of gases is defined as the volume which can be occupied by the gas alone in a container under specific pressure and temperature.

$$V_1 = n_1 \left(\frac{RT}{P} \right), \quad V_2 = n_2 \left(\frac{RT}{P} \right), \quad V_3 = n_3 \left(\frac{RT}{P} \right) \quad (1)$$

By summation of the last three equations, we get:

$$V_1 + V_1 + V_1 = (n_1 + n_2 + n_3) \left(\frac{RT}{P} \right) \quad (2)$$

$$V_1 + V_1 + V_1 = n \left(\frac{RT}{P} \right) \quad (3)$$

By comparison equation (3) with the universal gas equation:

$$PV = nRT \quad (4)$$

$$V = V_1 + V_1 + V_1 \quad (5)$$

Equation (5) represents Amagat's law of molar gas volumes.

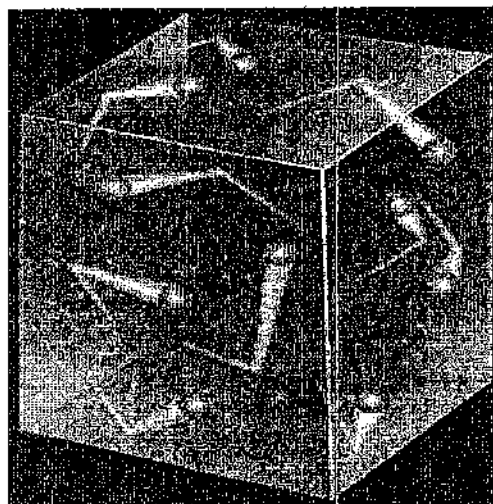
Dividing equation (1) to equation (4), we get:

$$V_i = X_i V$$

Kinetic Molecular Theory of Gases

Maxwell and Boltzmann (1859) developed a mathematical theory to explain the behaviour of gases and the gas laws. It is based on the fundamental concept that a gas is made of a large number of molecules in perpetual motion. Hence the theory is called the kinetic molecular theory or simply the kinetic theory of gases (The word kinetic implies motion). The kinetic theory makes the following assumptions.

1. Gases are composed of small molecules that are in constant, random motion.
2. The volume of the molecules is insignificant compared with the volume occupied by the gas.
3. Forces between the molecules are negligible, except when the molecules collide with one another.
4. Molecular collisions are perfectly elastic; that is, no energy is lost when the molecules collide.
5. The average kinetic energy of the gas molecules are directly proportional to the absolute temperature of the gas.



Postulates or Assumptions of Kinetic Theory of Gases

(1) Gases consist of of extremely small identical discrete particles called molecules of the same mass (m) as shown in Figure (12).

The actual volume of the molecules is negligible compared to the total volume of the gas.

(2) Gas molecules are in constant random motion with high velocities. They move in straight lines with uniform velocity and change direction on collision with other molecules or the walls of the container.

(3) The distance between the molecules is very large and it is assumed that van der Waals attractive forces between them do not exist. Thus the gas molecules can move freely, independent of each other. Therefore, attraction or repulsion forces between gas molecules are negligible.

(4) All collisions are perfectly elastic. Hence, there is no loss of the kinetic energy of a molecule during a collision.

(5) The pressure of a gas is caused by the hits recorded by molecules on the walls of the container.

(6) The average kinetic energy of the gas molecules is directly proportional to absolute temperature (Kelvin temperature). This implies that the average kinetic energy of molecules is the same at a given temperature.

The gas molecules interact only when they collide.

Average kinetic energy (K.E.) of molecules depends on absolute

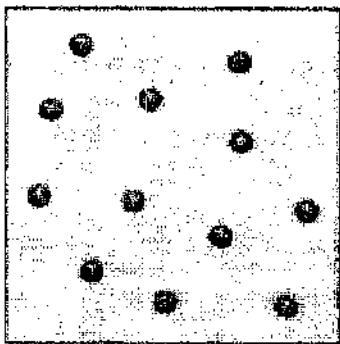


Figure (12 A)

A gas is made of molecules dispersed in space in the container.

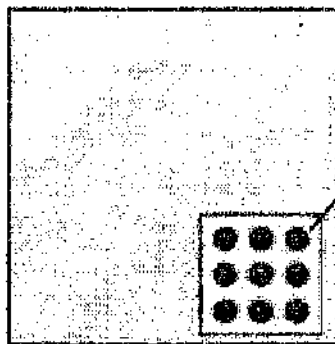


Figure (12 B)

Actual volume of the gas molecules is negligible

Figure (12) illustrate the negligible gas volume with comparison with the container vessel

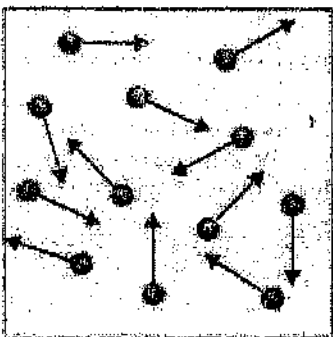


Figure (12 C)

Gas molecules are in constant motion in all possible directions.

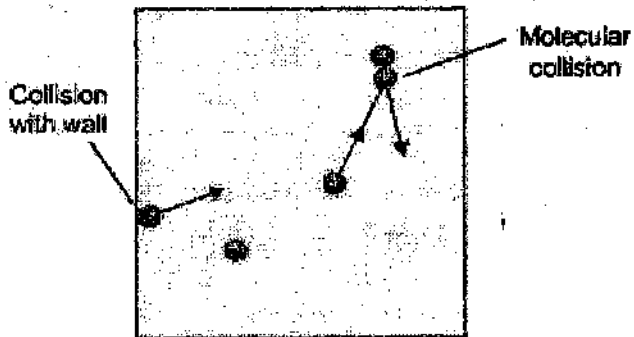


Figure (12 D)

Molecules move in straight line and change direction on collision with another molecule or wall of container.

Figure (12) Illustrate the gas molecules are in random and continuous movement with full elasticity

DERIVATION OF KINETIC GAS EQUATION

Starting from the postulates of the kinetic molecular theory of gases we can develop an important equation. This equation expresses PV of a gas in terms of the number of molecules, molecular mass and molecular velocity. This equation which we shall name as the Kinetic Gas Equation may be derived by the following clauses.

Let us consider a certain mass of gas enclosed in a cubic box (Fig. 14) at a fixed temperature.

the length of each side of the box = l cm

the total number of gas molecules = n

the mass of one molecule = m

the velocity of a molecule = v

The kinetic gas equation may be derived by the following steps :

(1) Resolution of Velocity of a Single Molecule along X, Y and Z Axes

According to the kinetic theory, a molecule of a gas can move with velocity v in any direction.

Velocity is a vector quantity and can be resolved into the components v along the X, Y and Z axes. These components are related to the velocity v by the following expression.

$$V^2 = v_x^2 + v_y^2 + v_z^2$$

Now we can consider the motion of a single molecule moving with the component velocities independently in each direction.

(2) The Number of Collisions per Second on Face A Due to One Molecule

Consider a molecule moving in X-direction between opposite faces A and B. It will strike the face A with velocity v_x and rebound with velocity $-v_x$ as shown in figure (14). To hit the same face again, the molecule must travel l cm to collide with the opposite face B and then again l cm to return to face A. Therefore, the time between two collisions of face A $\Delta t = \frac{2l}{v_x}$ seconds

No. of collisions per second on face A = $\frac{v_x}{2l}$

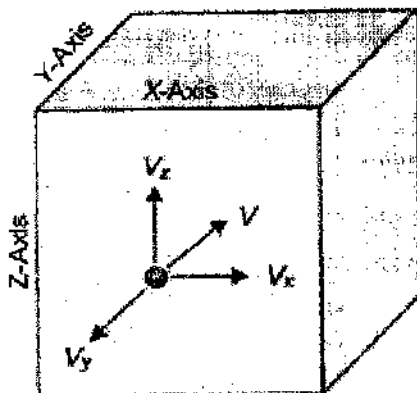


Figure (14)

Resolution of velocity v into Components V_x , V_y and V_z

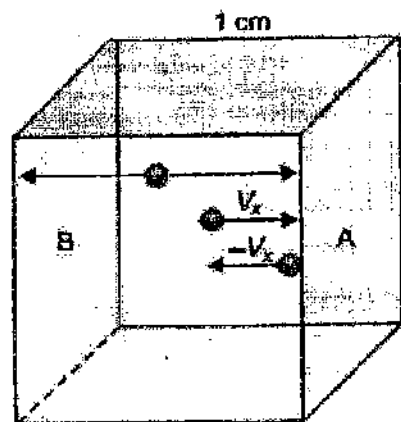


Figure (15)

Cubic box showing molecular collisions along axis

(3) The Total Change of Momentum on All Faces of the Box Due to One Molecule Only

Each impact of the molecule on the face A causes a change of momentum (mass $\times$ velocity):

$$\text{Momentum before the impact} = mv_x$$

$$\text{Momentum after the impact} = m(-v_x)$$

$$\therefore \text{Total change of momentum} = mv_x - (-mv_x) = 2mv_x$$

But the number of collisions per second on face A due to one molecule = $\frac{v_x}{2l}$

Therefore, the total change of momentum per second on face A caused by one molecule = $2mv_x \cdot \frac{v_x}{2l} = \frac{mv_x^2}{l}$

The change of momentum on both the opposite faces A and B along X-axis would be double i.e., $\frac{2mv_x^2}{l}$ similarly, the change of momentum along Y-axis and Z-axis will be $\frac{2mv_y^2}{l}$ and $\frac{2mv_z^2}{l}$ respectively. Hence, the overall change of momentum per second on all faces of the box will be:

$$\text{Momentum change per second} = \frac{2mv_x^2}{l} + \frac{2mv_y^2}{l} + \frac{2mv_z^2}{l}$$

$$\text{Momentum change per second} = \frac{2m}{l} (v_x^2 + v_y^2 + v_z^2) = \frac{2mv^2}{l}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

(4) Total Change of Momentum Due to Impacts of All the Molecules on All Faces of the Box

Suppose there are N molecules in the box each of which is moving with a different velocity v_1, v_2, v_3 , etc. The total change of momentum due to impacts of all the molecules on all faces of the box

$$\text{Total change of momentum} = \frac{2m}{l} (\sqrt[2]{1} + \sqrt[2]{2} + \sqrt[2]{3} + \dots)$$

Multiplying and dividing by N , we have:

$$= \frac{2mN}{l} \left(\frac{\sqrt[2]{1} + \sqrt[2]{2} + \sqrt[2]{3} + \dots}{n} \right) = \frac{2mNu^2}{l}$$

Where: u^2 is the mean square velocity.

(5) Calculation of Pressure from Change of Momentum; Derivation of Kinetic Gas Equation

Since force may be defined as the change in momentum per second, we can write:

$$\text{Force} = \frac{2mNu^2}{l}$$

But

$$\text{Pressure} = \frac{\text{Total force}}{\text{Total area}}$$

$$P = \frac{2 m N u^2}{l} \times \frac{1}{6 l^2} = \frac{1}{3} \frac{m N u^2}{l^3}$$

Since l^3 is the volume of the cube, V , we have

$$P = \frac{1}{3} \frac{m N u^2}{V}$$

$$PV = \frac{1}{3} m N u^2$$

This is the fundamental equation of the kinetic molecular theory of gases. It is called the **Kinetic Gas equation**. This equation although derived for a cubical vessel, is equally valid for a vessel of any shape. The available volume in the vessel could well be considered as made up of a large number of infinitesimally small cubes for each of which the equation holds.

Significance of the term u , as stated in clause (4) u^2 is the mean of the squares of the individual velocities of all the N molecules of the gas. But $u = \sqrt{u^2}$. Therefore u is called the **Root Mean Square (or RMS) Velocity**.

DISTRIBUTION OF MOLECULAR VELOCITIES

While deriving Kinetic Gas Equation, it was assumed that all molecules in a gas have the same velocity. But it is not so. When any two molecules collide, one molecule transfers kinetic energy ($\frac{1}{2}mv^2$) to the other molecule. The velocity of the molecule which gains energy increases and that of the other decreases. Millions of such molecular collisions are taking place per second. Therefore, the velocities of molecules are changing constantly. Since the number of molecules is very large, a fraction of molecules will have the same particular velocity. In this way there is a broad distribution of velocities over different fractions of molecules. In 1860 *James Clark Maxwell* calculated the distribution of velocities from the laws of probability. He derived the following equation for the distribution of molecular velocities.

$$\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} e^{-\frac{Mc^2}{2RT}} C^2 dc$$

where:

dN_c = number of molecules having velocities between C and $(C+ dc)$

N = total number of molecules

M = molecular mass

T = temperature on absolute scale (K)

The relation stated above is called **Maxwell's law of distribution of velocities**. The ratio $\frac{dn}{c}$ gives the fraction of the total number of molecules having velocities between C and $(C+ dc)$. Maxwell plotted such fractions against velocity possessed by the molecules. The curves so obtained illustrate the salient features of Maxwell distribution of velocities.

Fig. 10.20. Shows the distribution of velocities in nitrogen gas, N_2 , at 300 K and 600 K. It will be noticed that:

- (1) A very small fraction of molecules has either very low (close to zero) or very high velocities.
- (2) Most intermediate fractions of molecules have velocities close to an average velocity represented by the peak of the curve. This velocity is called the most probable velocity. It may be defined as the velocity possessed by the largest fraction of molecules corresponding to the highest point on the Maxwellian curve.
- (3) At higher temperature, the whole curve shifts to the right (dotted curve at 600 K). This shows that at higher temperature more molecules have higher velocities and fewer molecules have lower velocities.

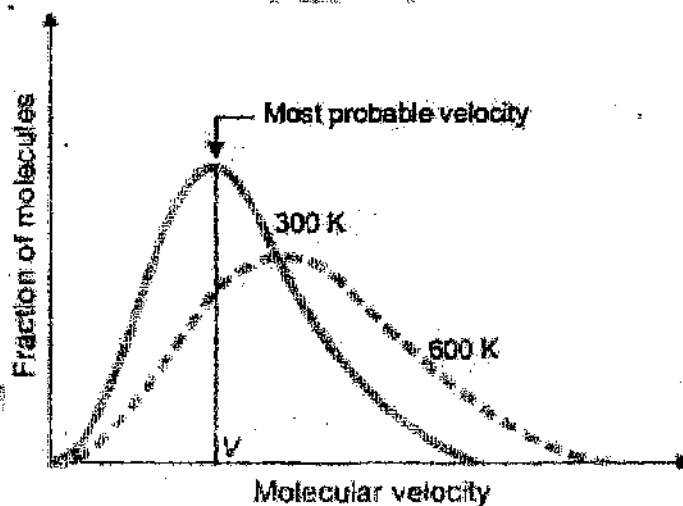


Figure 10.20 Distribution of molecular velocities in nitrogen gas, N_2 , at 300 K and 600 K.

DIFFERENT KINDS OF VELOCITIES

In our study of kinetic theory we come across three different kinds of molecular velocities:

- (1) the Average velocity (V)
- (2) the Root Mean Square velocity (μ)

(3) the Most Probable velocity (v_{mp})

Average Velocity

Let there be n molecules of a gas having individual velocities $v_1, v_2, v_3, \dots, v_n$. The ordinary average velocity is the arithmetic mean of the various velocities of the molecules

$$\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

From Maxwell equation it has been established that the average velocity v_{av} is given by the expression

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

Substituting the values of R , T , π and M in this expression, the average value can be calculated.

Root Mean Square Velocity

If $v_1, v_2, v_3, \dots, v_n$ are the velocities of n molecules in a gas, μ^2 , the mean of the squares of all the velocities is

$$\mu^2 = \frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}$$

Taking the root

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$$

μ is thus the **Root Mean Square velocity** or **RMS velocity**. It is denoted by u . The value of the RMS of velocity u , at a given temperature can be calculated from the Kinetic Gas Equation

$$PV = \frac{1}{2} mNu^2 \quad (\text{kinetic energy})$$

$$u^2 = \frac{3PV}{mN}$$

For one mole of gas

$$PV = RT$$

Therefore,

$$u^2 = \frac{3PV}{M}$$

M is the molar mass

$$u = \sqrt{\frac{3PV}{M}}$$

By substituting the values of R , T and M , the value of u (RMS velocity) can be determined. RMS velocity is superior to the average velocity considered earlier. With the help of u , the total Kinetic energy of a gas sample can be calculated.

Most Probable Velocity

As already stated the most probable velocity is possessed by the largest number of molecules in a gas. According to the calculations

made by Maxwell, the most probably velocity, v_{mp} is given by the expression.

$$V_{mps} = \sqrt{\frac{2RT}{M}}$$

Substituting the values of R, T and M in this expression, the most probably velocity can be calculated.

Relation between Average Velocity, RMS Velocity and Most

We know that the average velocity, $\bar{v}$, is given by the expression

$$\begin{aligned}\bar{v} &= \sqrt{\frac{8RT}{\pi M}} \quad \text{and} \quad \mu = \sqrt{\frac{3RT}{M}} \\ \therefore \frac{\bar{v}}{\mu} &= \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}} = 0.9213 \\ \bar{v} &= \mu \times 0.9213\end{aligned}$$

That is, Average Velocity = $0.9213 \times$ RMS Velocity

The expression for the most probably velocity, v_{mp} , is

$$\begin{aligned}v_{mp} &= \sqrt{\frac{2RT}{M}} \quad \text{and} \quad \mu = \sqrt{\frac{3RT}{M}} \\ \frac{v_{mp}}{\mu} &= \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165 \\ v_{mp} &= \mu \times 0.8165\end{aligned}$$

That is, Most Probable Velocity = $0.8165 \times$ RMS Velocity

RMS can be easily calculated by the application of Kinetic Gas equation. Knowing the value of RMS, we can find the average velocity and the most probable velocity from expressions (1) and (2).

CALCULATION OF MOLECULAR VELOCITIES

The velocities of gas molecules are exceptionally high. Thus, velocity of hydrogen molecule is $1838 \text{ metres sec}^{-1}$. While it may appear impossible to measure so high velocities, these can be easily calculated from the Kinetic Gas equation. Several cases may arise according to the available data.

While calculating different types of velocities, we can also make use of the following expressions stated already.

RMS velocity, $\mu = \sqrt{\frac{3RT}{M}}$

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

Most Probable velocity, $v_{mp} = \sqrt{\frac{2RT}{M}}$

Case1. Calculation of Molecular Velocity when temperature alone is given

$$PV = \frac{1}{3} mNu^2 \quad (\text{Kinetic gas equation})$$

Where $N = N_0$ (Avogadro's number)

Thus we have

$$M = m \times N_0 = \text{molecular mass of the gas}$$

$$u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} \quad (\because PV = RT \text{ for 1 mole})$$

But: $R = 8.314 \times 10^7 \text{ ergs deg}^{-1} \text{ mol}^{-1} = 0.8314 \times 10^8 \text{ ergs deg}^{-1} \text{ mol}^{-1}$

$$u = \sqrt{\frac{3 \times 0.8413 \times 10^8 \times T}{M}} = 1.58 \times 10^4 \sqrt{\frac{T}{M}} \text{ cm s}^{-1}$$

where, T is Kelvin temperature and M the molar mass.

Problem: Calculate the root mean square velocity of CO_2 molecule at 1000°C .

Solution:

$$T = 273 + 1000 = 1273 \text{ K} \text{ \& } M = 44 \text{ g/mol}$$

$$u = 1.58 \times 10^4 \sqrt{\frac{T}{M}} \text{ cm s}^{-1} = 1.58 \times 10^4 \sqrt{\frac{1273}{44}} = 84985 \text{ cm s}^{-1}$$

$$u = 849.85 \text{ m s}^{-1}$$

Case2. Calculation of Molecular Velocity when temperature and pressure both are given.

In such cases we make use of the following relation based on Kinetic Gas equation.

$$u = \sqrt{\frac{3PV}{M}}$$

We know that 1 mole of a gas at STP occupies a volume of 22400 ml (known as molar volume). But before applying this relation the molar volume is reduced to the given conditions of temperature and pressure

Problem: Calculate the RMS velocity of chlorine molecules at 12°C and 78 cm Hg pressure.

Solution:

St STP	At given conditions
$V_1 = 22400 \text{ ml}$	$V_2 = ?$
$T_1 = 273 \text{ K}$	$T_2 = 12 + 273 \text{ K}$
$P_1 = 76 \text{ cm Hg}$	$P_2 = 78 \text{ cm Hg}$

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

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{76 \text{ cm Hg} \times 22400 \text{ ml} \times 285 \text{ K}}{273 \text{ K} \times 78 \text{ cm Hg}} = 22785 \text{ ml}$$

$$u = \sqrt{\frac{3PV}{M}}$$

$$P = h \rho g = 78 \text{ cm Hg} \times 13.6 \text{ g cm}^{-3} \times 981 \text{ m s}^{-2} = 1040644.8 \text{ dynes cm}^{-2}$$

$$V = 22785 \text{ ml}; \quad M = 71 \text{ g/mol}$$

$$u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times 78 \text{ cm Hg} \times 13.6 \text{ g cm}^{-3} \times 981 \text{ m s}^{-2} \times 22785 \text{ ml}}{71 \text{ g mol}^{-1}}}$$

$$u = 31652 \text{ cm sec}^{-1} \text{ or } 316.52 \text{ m sec}^{-1}$$

Case 3. Calculation of Molecular Velocity at STP

Here we use the relation

$$u = \sqrt{\frac{3PV}{M}}$$

where:

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$V = 22400 \text{ ml}$$

M = Molar mass of the gas

Problem: Calculate the average velocity of nitrogen molecule at STP.

Solution:

In this example we have,

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$V = 22400 \text{ ml}$$

$$M = 28 \text{ g/mol}$$

Substituting these values in the equation

$$u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times 76 \text{ cm Hg} \times 13.6 \text{ g cm}^{-3} \times 981 \text{ m s}^{-2} \times 22400 \text{ ml}}{28 \text{ g mol}^{-1}}}$$

$$u = 49330 \text{ cm s}^{-1}$$

$$\therefore \text{Average velocity} = 0.9213 \times 49330 \text{ cm s}^{-1} = 45447 \text{ cm s}^{-1}$$

Case 4. Calculation of Molecular Velocity when pressure and density are given

In this case we have

$$u = \sqrt{\frac{3PV}{M}} \quad \text{or} \quad u = \sqrt{\frac{3P}{D}} \quad \left[\frac{M}{V} = D \right]$$

where, P is expressed in dynes cm^{-2} and D in gm ml^{-1}

Problem: Oxygen at 1 atmosphere pressure and 0.0°C has a density of 1.4290 grams per litre. Find the RMS velocity of oxygen molecules.

Solution:

We have: $P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$

$$d = 1.4290 \text{ g L}^{-1} = \frac{1.4290 \text{ g}}{1000 \text{ ml}} = 0.001429 \text{ g ml}^{-1}$$

$$\mu = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001429}} = 461.38 \text{ cm s}^{-1}$$

COLLISION PROPERTIES

In the derivation of Kinetic gas equation we did not take into account collisions between molecules. The molecules in a gas are constantly colliding with one another. The transport properties of gases such as diffusion, viscosity and mean free path depend on molecular collisions. We will now discuss some properties of gases which determine the frequency of collisions.

The Mean Free Path

At a given temperature, a molecule travels in a straight line before collision with another molecule. The distance travelled by the molecule before collision is termed free path. The free path for a molecule varies from time to time. The mean distance travelled by a molecule between two successive collisions is called the Mean Free Path. It is denoted by λ . If ℓ_1, ℓ_2, ℓ_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{\ell_1 + \ell_2 + \ell_3 + \dots + \ell_n}{n}$$

where n is the number of molecules with which the molecule collides. Evidently, the number of molecular collisions will be less at a lower pressure or lower density and longer will be the mean free path. The mean free path is also related with the viscosity of the gas

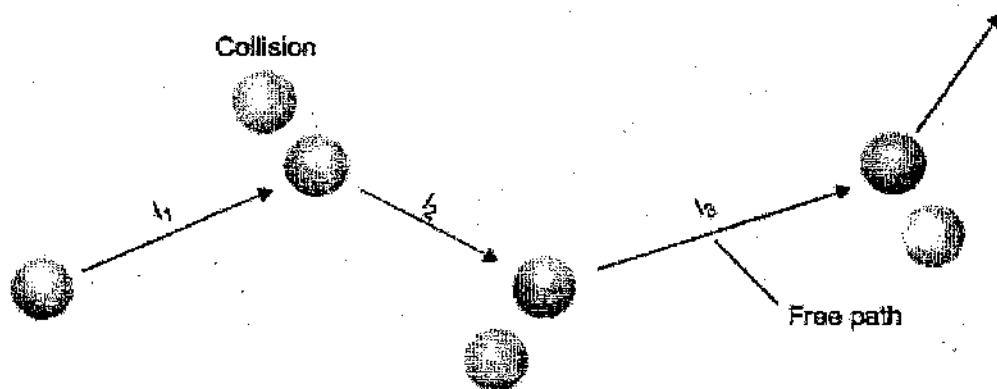


Figure 10.-21 The mean free path illustrated.

The mean free path, λ , is given by the expression

$$\lambda = \eta \sqrt{\frac{3}{Pd}}$$

where

P = pressure of the gas

d = density of the gas

η = coefficient of viscosity of the gas

By a determination of the viscosity of the gas, the mean free path can be readily calculated. At STP, the mean free path for hydrogen is 1.78×10^{-5} cm and for oxygen it is 1.0×10^{-5} cm.

Effect of Temperature and Pressure on Mean Free Path

(a) Temperature

The ideal gas equation for n moles of a gas is

$$n = \frac{\text{number of molecules}}{\text{Avogadro's Number}} = \frac{N}{N_0}$$

Substituting this in equation (i) we get:

$$PV = \frac{N}{N_0} RT \quad (i)$$

or:

$$\frac{N}{V} = \frac{PN_0}{RT}$$

At constant pressure

$$N \propto \frac{1}{T} \quad (ii)$$

The mean free path is given by:

$$\lambda = \frac{\text{Distance travelled by the molecule per second}}{\text{Number of collision per c.c.}} = \frac{\bar{v}}{\sqrt{2} \pi \sigma^2 \bar{v} \bar{N}}$$

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \bar{N}} \quad (iii)$$

combining equations (ii) and (iii), we get

$$\lambda \propto T$$

Thus, the mean free path is directly proportional to the absolute temperature.

(b) Pressure

We know that the pressure of a gas at certain temperature is directly proportional to the number of molecules per c.c. i.e

$$P \propto \bar{N}$$

and mean free path is given by

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \bar{N}}$$

Combining these two equations, we get

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

Thus, the mean free path of a gas is directly proportional to the pressure of a gas at constant temperature.

Problem: At 0.0°C and 1 atmospheric pressure the molecular diameter of a gas is $4\text{\AA}$. Calculate the mean free path of its molecule.

Solution: The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \bar{N}}$$

Where: σ is the molecular diameter and $\bar{N}$ is the No of molecules per c.c

Here

$$\sigma = 4\text{\AA} = 4 \times 10^{-8} \text{ cm}$$

We know 22400 ml of a gas 0.0°C and 1 atm. pressure contains 6.02×10^{23} molecules.

$$\therefore \text{No. of molecules per c.c., } \bar{N} = \frac{6.02 \times 10^{23}}{22400} = 2.689 \times 10^{19} \text{ molecules}$$

Substituting the values, we get

$$\sigma = \frac{1}{1.414 \times 3.14 \times (4 \times 10^{-8})^2 \times 2.689 \times 10^{19}} = \frac{1}{1.414 \times 3.14 \times 16 \times 2.689 \times 10^3}$$
$$\sigma = 0.524 \times 10^{-5} \text{ cm}$$

Problem: The root mean square velocity of hydrogen at STP is $1.83 \times 10^5 \text{ cm s}^{-1}$ and its mean free path is $1.78 \times 10^{-5} \text{ cm}$. Calculate the collision number at STP.

Solution: Here root mean square velocity

$$\mu = 1.831 \times 10^5 \text{ cm s}^{-1}$$

We know average velocity $\bar{v} = 0.9213 \times \text{RMS velocity}$

$$\text{average velocity } \bar{v} = 0.9213 \times 1.831 \times 10^5 \text{ cm} = 1.6869 \times 10^5 \text{ cm sec}^{-1}$$

$$\text{The mean free path} = \frac{\text{Average velocity}}{\text{Collision number}}$$

$$\therefore \text{Collision number} = \frac{\text{Average velocity}}{\text{Mean free path}} = \frac{1.6869 \times 10^5 \text{ cm s}^{-1}}{1.78 \times 10^{-5} \text{ cm}}$$

$$\text{Collision number} = 9.4769 \times 10^9 \text{ s}^{-1}$$

The Collision Diameter

When two gas molecules approach one another, they cannot come closer beyond a certain distance. The closest distance between the centres of the two molecules taking part in a collision is called the Collision Diameter. It is denoted by σ whenever the distance between the centres of two molecules is σ , a collision occurs.

The collision diameter is obviously related to the mean free path of molecules. The smaller the collision or molecular diameter, the larger is the mean free path.

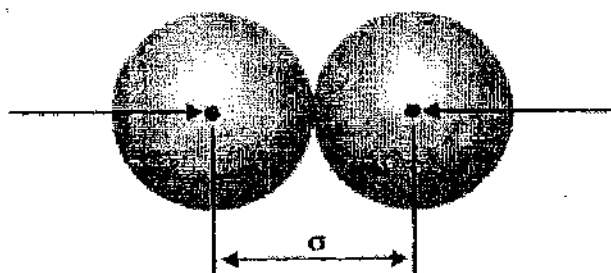


Figure 10.22 Collision diameter of molecules.

The collision diameter can be determined from viscosity measurements. The collision diameter of hydrogen is 2.74 Å and that of oxygen is 3.61 Å.

The Collision Frequency

The collision frequency of a gas is defined as:

The number of molecular collisions taking place per second per unit volume (c.c.) of the gas.

Let a gas contain N molecules per c.c. From kinetic consideration it has been established that the number of molecules, n , with which a single molecule will collide per second, is given by the relation

$$n = \sqrt{2} \pi \bar{v} \sigma^2 N$$

where: $\bar{v}$ = average velocity; σ = collision diameter.

If the total number of collisions taking place per second is denoted by Z , we have

$$Z = \sqrt{2} \pi \bar{v} \sigma^2 N \times N = \sqrt{2} \pi \bar{v} \sigma^2 N^2$$

Since each collision involves two molecules, the number of collision per second per c.c. of the gas will be $Z/2$

$$\text{Hence the collision frequency} = \frac{\sqrt{2} \pi \bar{v} \sigma^2 N^2}{2} = \frac{\pi \bar{v} \sigma^2 N^2}{\sqrt{2}}$$

Evidently, the collision frequency of a gas increases with increase in temperature, molecular size and the number of molecules per c.c.

Effect of Temperature and Pressure on Collision Frequency

(i) Effect of Temperature

We know collision frequency is given by

$$Z = \frac{\pi \bar{v} \sigma^2 N^2}{\sqrt{2}} \quad (i)$$

From this equation it is clear that

$$Z \propto \bar{v}$$

but:

$$\mu \propto \sqrt{T} \quad \text{or} \quad Z \propto \sqrt{T}$$

Hence collision frequency is directly proportional to the square root of absolute temperature.

(ii) Effect of Pressure

From equation (i), we have:

$$Z \propto \bar{N}^2 \quad (ii)$$

Where $\bar{N}$ is the number of molecules per c.c. But we know that the pressure of the gas at a certain temperature i.e.

$$P \propto \bar{N} \quad (iii)$$

combining equation (ii) and (iii) we get

$$Z \propto P^2$$

Thus the collision frequency is directly proportional to the square of the pressure of the gas.

SPECIFIC HEAT RATIO OF GASES

The Specific heat is defined as the amount of heat required to raise the temperature of one gram of a substance through 1°C. It may be measured at constant volume or at a constant pressure and though the difference in the two values is negligible in case of solids and liquids, it is appreciable in case of gases and a ratio of the two values gives us valuable information about the atomicity of a gas molecule.

Specific Heat at Constant Volume

It is the amount of heat required to raise the temperature of one gas through 1°C while the volume is kept constant and the pressure allowed increasing. It is denoted by the symbol C_v . In Physical Chemistry it is more common, however, to deal with one gram mole of the gas and the heat required in such case is called

Molecular Heat and is represented at constant volume by C_v . It is possible to calculate its value by making use of the Kinetic theory. Consider one mole of a gas at the temperature T . Its kinetic energy is $\frac{1}{2}mnu^2$. From the kinetic gas equation

$$PV = \frac{1}{2} mnu^2 = \frac{2}{3} \times \frac{1}{2} mnu^2 = RT$$

$$\frac{1}{2} mnu^2 (= KE) = \frac{3}{2} RT$$

If the temperature is raised by 1°C to $(T+1)$ K kinetic energy becomes $\frac{3}{2} R(T+1)$.

$$\therefore \text{Increase in kinetic energy} = \frac{3}{2} R(T+1) - \frac{3}{2} RT = \frac{3}{2} R$$

If, therefore, it be assumed that the heat supplied to a gas at constant volume is used up entirely in increasing the kinetic energy of the moving molecules, and consequently increasing the temperature, the value of C_v should be equal $\frac{3}{2} RT$. It is actually so for monoatomic gases and vapours because such molecules can execute only translatory motion along the three co-ordinate axes. Motion of monoatomic gas molecules is the simplest and can be resolved into three perpendicular components along the co-ordinate axes. Thus the energy of such a molecule can be considered to be composed of three parts as

$$\frac{1}{2} mv^2 = \frac{1}{2} mv_x^2 + \frac{1}{2} mv_y^2 + \frac{1}{2} mv_z^2$$

The number of square terms involved in determining the total kinetic energy of a molecule is often referred to as the **Degrees of freedom of motion**. Such molecules have three degrees of freedom of motion. According to the principle of equipartition of energy, total energy of the molecule is equally distributed among all its degrees of freedom. But in the case of diatomic and polyatomic molecules, the heat supplied may not only increase this **kinetic energy of translation** of the molecules as a whole but also cause an increase in the energy in the inside of the molecules which we may call as **intramolecular energy**. This intramolecular energy may be the **vibration energy** i.e., energy of the atoms executing vibrations with respect to each other along their line of centres or **rotational energy** which manifests itself in the rotation of the molecules about axes perpendicular to the line of centres. There will be needs will be complex and are denoted by 'x' - a factor which depends upon vibrational and rotational degrees of freedom. Vibrational degrees of freedom rapidly increase with the increase in the total number of atoms in a molecule but the degrees of freedom are two

for linear diatomic and three for nonlinear diatomic molecules in case of rotational motion.

Consequently in such cases the molecular heat will be greater than $\frac{3}{2}R$ by the factor x .

or
$$C_v = \frac{3}{2}R + x$$

The value of x varies from gas to gas and is zero for monoatomic molecules.

Specific Heat at Constant Pressure

It may be defined as the amount of heat required to raise the temperature of one gram of gas through 1°C , the pressure remaining constant while the volume is allowed to increase. It is written as C_p and the Molecular heat in this gas is represented as C_p .

Now, whenever a gas expands it has to do work against external pressure. It means that when a gas is heated under constant pressure, the heat supplied is utilised in two ways:

(1) in increasing the kinetic energy of the moving molecules and this has already been shown to be equal to $\frac{3}{2}R + x$ cal.

(2) in performing external work done by the expanding gas. The work done by the gas is equivalent to the product of the pressure and the change in volume. Let this change in volume be ΔV when the constant pressure is P and the initial volume is V .

For 1 g mole of the gas at temperature T ,

$$PV = RT \quad (i)$$

At temperature $(T+1)$ K:

$$P(V + \Delta V) = R(T + 1) \quad (ii)$$

Subtracting (i) from (ii):

$$P \times \Delta V = R$$

Hence R cal must be added to the value of $\frac{3}{2}R$ cal in order to get the thermal equivalent of the energy supplied to one gram mole of the gas in the form of heat when its temperature is raised by 1°C .

$$C_p = \frac{3}{2}R + R = \frac{5}{2}R \quad (\text{for monoatomic molecules})$$

For di- and polyatomic molecules, it will be $\frac{3}{2}R + x$.

Specific Heat Ratio

The ratio of the molecular heats will be the same as the ratio of the specific heats. It is represented by the symbol γ .

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + x}{\frac{3}{2}R + x}$$

For monoatomic molecules, $x = 0$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.667$$

For diatomic molecules in most cases, $x = R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$$

For polyatomic molecules, very often $x = \frac{3}{2}R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + \frac{3}{2}R}{\frac{3}{2}R + \frac{3}{2}R} = \frac{8}{6} = 1.33$$

These results are found to be in accord with experimental observations at 15°C given in the Table that follows and thus specific heat ratio helps us to determine the atomicity of gas molecules. The theoretical difference between C_p and C_v as calculated above is R and its observed value also shown in the table below comes out to about 2 calories.

Gas	C_p	C_v	$C_p - C_v = R$	$\gamma = \frac{C_p}{C_v}$	Atomicity
Helium	5.00	3.01	1.99	1.661	1
Argon	4.97	2.98	1.90	1.667	1
Mercury vapour	6.93	2.94	1.99	1.40	2
Nitrogen	6.95	2.96	1.99	1.40	2
Oxygen	6.82	4.83	1.49	1.41	2
Carbon dioxide	8.75	6.71	2.04	1.30	3
Hydrogen sulphide	8.62	6.53	2.09	1.32	3

DEVIATIONS FROM IDEAL BEHAVIOUR

An ideal gas is one which obeys the gas laws or the gas equation $PV = RT$ at all pressures and temperatures. However no gas is ideal. Almost all gases show significant deviations from the ideal behaviour. Thus the gases H_2 , N_2 and CO_2 which fail to obey the ideal-gas equation are termed nonideal or real gases.

Compressibility Factor

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the **Compressibility factor**, denoted by Z . It is defined as:

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

The deviations from ideality may be shown by a plot of the compressibility factor, Z , against P .

For an ideal gas, $Z = 1$ and it is independent of temperature and pressure. The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1. The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of nonideality of the gas.

For a real gas, the deviations from ideal behaviour depend on (i) pressure; and temperature. This will be illustrated by examining the compressibility curves of some gases discussed below with the variation of pressure and temperature.

Effect of Pressure Variation on Deviations

Figure (16) shows the compressibility factor, Z , plotted against pressure for H_2 , N_2 and CO_2 at a constant temperature.

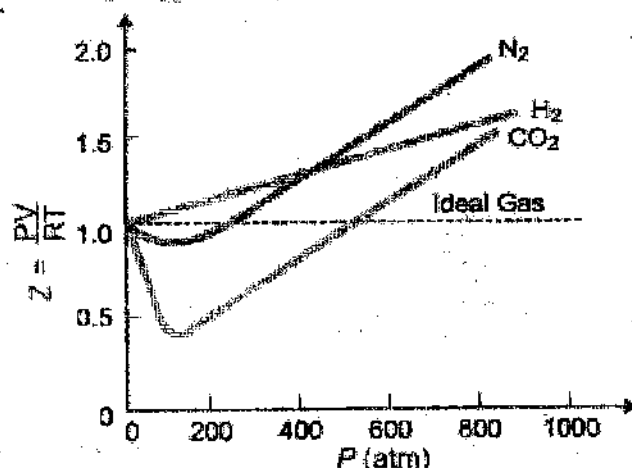


Figure (16) Z versus P plots for H_2 , N_2 and CO_2 at 300 K.

At very low pressures (upto 10 atm), real gases exhibit nearly ideal behaviour. As the pressure is increased, H_2 shows a continuous increase in Z (from $Z = 1$). Thus the H_2 curve lies above the ideal gas curve at all pressures.

For N_2 and CO_2 , Z first decreases ($Z < 1$). It passes through a minimum and then increases continuously with pressure ($Z > 1$). For a gas like CO_2 the dip in the curve is greatest as it is most easily liquefied.

Effect of Temperature on Deviations

Figure (17) shows plots of Z or PV/RT against P for N_2 at different temperatures. It is clear from the shape of the curves that the deviations from the ideal gas behaviour become less and less with increase of temperature. At lower temperature, the dip in the curve is large and the slope of the curve is negative. That is, $Z < 1$. As the temperature is raised, the dip in the curve decreases. At a certain temperature, the minimum in the curve vanishes and the curve remains horizontal for an appreciable range of pressures. At this temperature, PV/RT is almost unity and the Boyle's law is obeyed. Hence this temperature for the gas is called Boyle's temperature. The Boyle temperature of each gas is characteristic e.g., for N_2 it is 332 K.

Conclusions

From the above discussions we conclude that:

- (1) At low pressures and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.
- (2) At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.
- (3) The closer the gas is to the liquefaction point; the larger will be the deviation from the ideal behaviour.

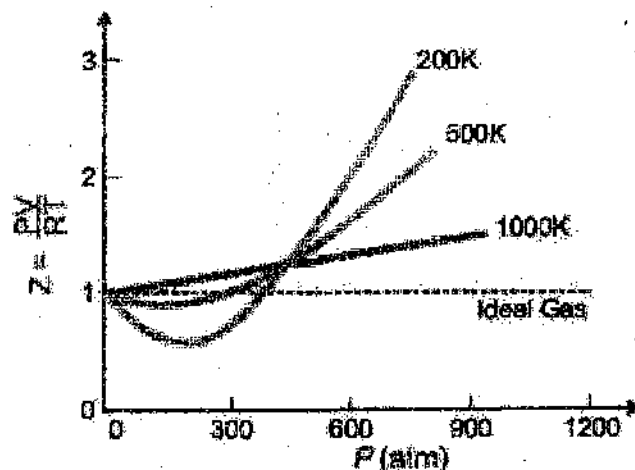


Figure (17) Z versus P plots for N_2 at different temperatures.

Explanation of Deviation of van der Waals equation:

van der Waals (1873) attributed the deviations of real gases from ideal behaviour to two erroneous postulates of the kinetic theory. These are:

(1) the molecules in a gas are point masses and possesses no volume.

(2) there are no intermolecular attractions in a gas.

Therefore, the ideal gas equation $PV = nRT$ derived from kinetic theory could not hold for real gases. *van der Waals* pointed out that both the pressure (P) and volume (V) factors in the ideal gas equation needed correction in order to make it applicable to real gases.

Volume Correction

The volume of a gas is the free space in the container in which molecules move about. Volume V of an ideal gas is the same as the volume of the container. The dot molecules of ideal gas have zero-volume and the entire space in the container is available for their movement. However, *van der Waals* assumed that molecules of a real gas are rigid spherical particles which possess a definite volume.

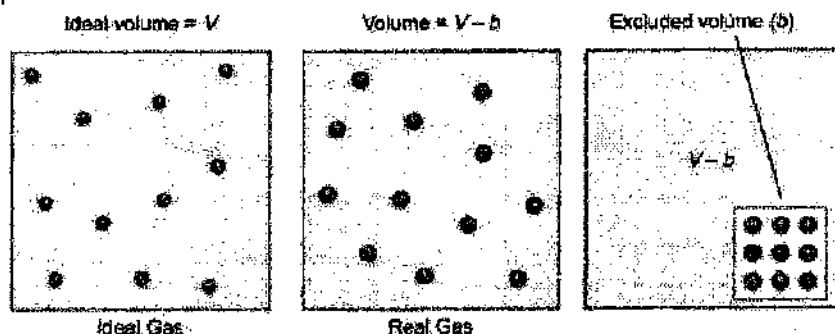


Figure (18) Volume of a Real gas

The volume of a real gas is, therefore, ideal volume minus the volume occupied by gas molecules (Figure 18). If b is the effective volume of molecules per mole of the gas, the volume in the ideal gas equation is corrected as: $(V - b)$

For n moles of the gas, the corrected volume is: $(V - nb)$

where b is termed the **excluded volume** which is constant and characteristic for each gas.

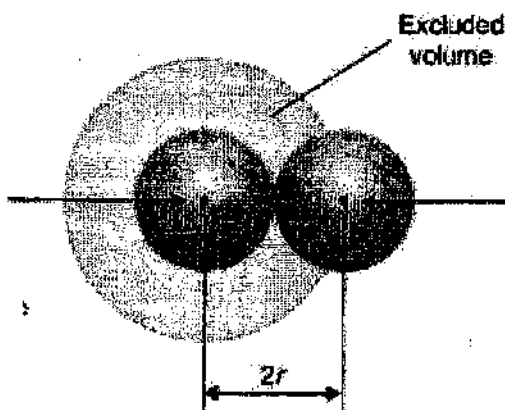


Figure (19) Excluded volume for a pair of gas molecules

Excluded volume is four times the actual volume of molecules. The excluded volume is not equal to the actual volume of the gas molecules. In fact, it is four times the actual volume of molecules and can be calculated as follows.

Let us consider two molecules of radius r colliding with each other (Figure 19). Obviously, they cannot approach each other closer than a distance $(2r)$ apart. Therefore, the space indicated by the dotted sphere having radius $(2r)$ will not be available to all other molecules of the gas. In other words the dotted spherical space is excluded volume per pair of molecules. Thus,

$$\text{Excluded volume for two molecules} = \frac{4}{3} \pi (2r)^3 = 8 \left(\frac{4}{3} \pi r^3 \right)$$

$$\text{Excluded volume per molecule (V}_e\text{)} = \frac{1}{2} \times 8 \left(\frac{4}{3} \pi r^3 \right) = 4 V_m$$

Where: V_m is the actual volume of a single molecule.

Therefore, in general, excluded volume of the gas molecules is four times the actual volume of molecules.

Pressure Correction

A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull (Figure 20). Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas, P , will be less than the ideal pressure. If the actual pressure P , is less than P_{ideal} by a quantity p , we have:

$$P = P_{\text{ideal}} - p$$

or

$$P_{\text{ideal}} = P + p$$

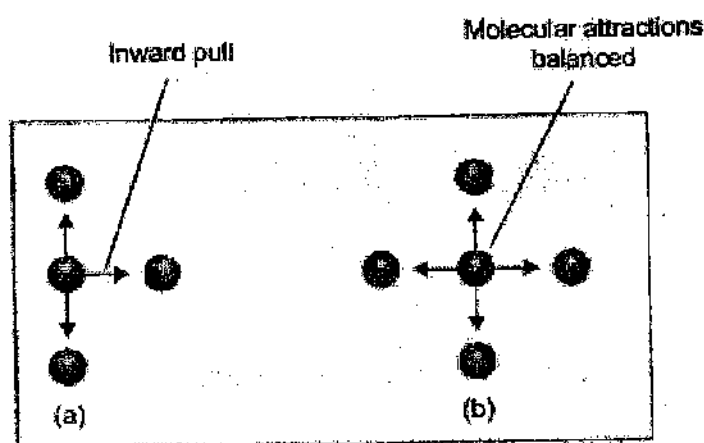


Figure (20)

- (a) A molecule about to strike the wall has a net inward pull;
- (b) A molecule in the interior of gas has balanced attractions.

p is determined by the force of attraction between molecules (A) striking the wall of container and the molecules (B) pulling them inward. The net force of attraction is, therefore, proportional to the concentration of (A) type molecules and also of (B) type of molecules. That is,

$$p \propto C_A \times C_B$$

or

$$p \propto \frac{n}{V} \times \frac{n}{V}$$

or

$$p = \frac{a n^2}{V^2}$$

where n is total number of gas molecules in volume V and a is proportionality constant characteristic of the gas. Thus the pressure P in the ideal gas equation is corrected as:

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

for n moles of gas.

van der Waals Equation

Substituting the values of corrected pressure and volume in the ideal gas equation, $PV = nRT$, we have

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

This is known as **van der Waals equation** for n moles of a gas. For 1 mole of a gas ($n = 1$), van der Waals equation becomes

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

Constant a and b in van der Waals equation are called **van der Waals constants**. These constants are characteristic of each gas.

Determination of a and b

From the expression (1), the value of a is given by the relation

$$a = \frac{p V^2}{n^2}$$

If the pressure is expressed in atmospheres and volume in litres,

$$a = \frac{(\text{pressure}) (\text{volume})^2}{(\text{mol})^2} = \frac{\text{atm L}^2}{\text{mol}^2} = \text{atm L}^2 \text{ mol}^{-2}$$

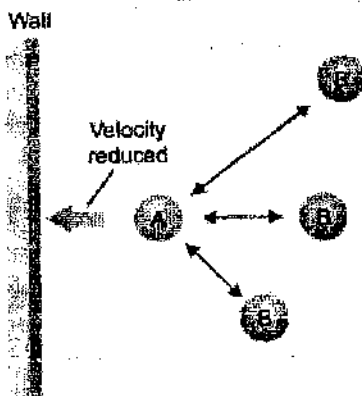


Figure (21) The striking molecule A is pulled inward by molecules B which reduces the velocity of A and causes the decrease of pressure

Thus a is expressed in **atm litre² mol⁻²** units.

Since nb is excluded volume for n moles of gas,

$$b = \frac{\text{volume}}{n} = \frac{\text{L}}{\text{mol}} = \text{L mol}^{-1}$$

If volume is expressed in litres, b is expressed in **litre mol⁻¹** units.

SI units of a and b . If pressure and volume are taken in SI units, we have:

$$a = \frac{(\text{pressure}) (\text{volume})^2}{(\text{mol})^2} = \frac{(\text{Nm}^{-2}) (\text{m}^3)^2}{(\text{mol})^2} = \text{N m}^4 \text{ mol}^{-2}$$

and

$$b = \text{Volume mol}^{-1} = \text{m}^3 \text{mol}^{-1}$$

The equation of van der Waals can explain the general behaviour of gases more correctly than the ideal equation $PV = RT$.

(1) **At very small pressures:** Volume (V) of the gas is very large and both correction terms $\left(\frac{a}{V^2}\right)$ and (b) are negligible according to Boyle's law. It states that: "At constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure". Therefore the van der Waals gas equation is reduced to $PV = RT$ for one mole of the gas.

(2) **At slightly higher pressure:** The term (b) is neglected compared with the volume (V) and equation of van der Waals is reduced to for one mole of the gas:

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

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

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

Thus the value of PV is less than the ideal value by $\left(\frac{a}{V^2}\right)$ and the decrease in the value of PV increase with the increase of pressure. This explains the falling branch in the $PV - P$ isotherm as illustrated in figure (22).

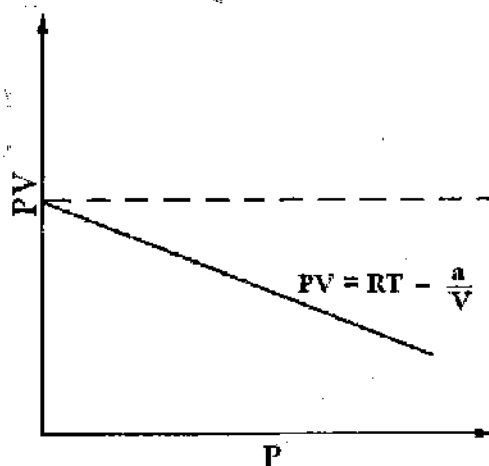


Figure (22) Effect of slightly higher pressure on van der Waals isotherm

(3) **At higher pressures:** The effect of attraction forces is negligible compared with the effect of the volume of molecules. Thus, van der Waals equation for one mole of the gas is reduced to:

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

$$PV = RT + Pb$$

Thus PV is greater than ideal gas value by (Pb) and increase in its value increases with increase of the pressure. Therefore, the increase in (PV) after the minimum in the $PV - P$ isotherms is due to the effect of the term (b) . This explains the rising branch of the $(PV - P)$ isotherm as illustrated in Figure (23). In case of hydrogen (H_2) and helium (He) gases the value (a) is very small compared with the value (b) even at small pressures. That is why PV increases continuously with pressure at ordinary temperature.

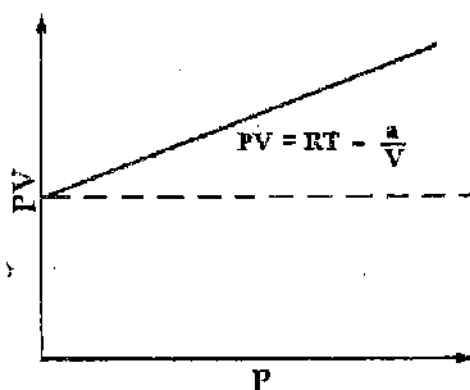


Figure (23) Effect of high pressure on van der Waals isotherm

Solved Problem: Calculate the pressure exerted by 1.00 mole of methane (CH_4) in a 250 mL container at 300 K using van der Waals equation. What pressure will be predicted by ideal gas?

$a = 2.253 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.0428 \text{ L mol}^{-1}$; $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$.

Solution:

van der Waals equation: $\left(P + \frac{an^2}{V^2}\right) (V-nb) = nRT$

Dividing by $(V - nb)$ and solving for P :

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

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

Substituting $n = 1$, $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$, $V = 0.250 \text{ L}$, $T = 300 \text{ K}$ and the values of a and b , we have:

$$P = \frac{1.0 \text{ mol} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.25 \text{ L} - (1 \times 0.0428 \text{ L mol}^{-1})} - \frac{2.253 \text{ L}^2 \text{ atm mol}^{-2} \times (1)^2}{(0.25 \text{ L})^2}$$

$$P = 82.8 \text{ atm}$$

The ideal gas equation predicts that:

$$P = \frac{nRT}{V} = \frac{1.0 \text{ mol} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.250 \text{ L}} = 98.5 \text{ atm}$$

Graham's Law of Diffusion:

When two gases are placed in contact, they mix spontaneously. This is due to the movement of molecules of one gas into the other gas. This process of mixing of gases by random motion of the molecules is called Diffusion. Thomas Graham observed that molecules with smaller masses diffused faster than heavy molecules.



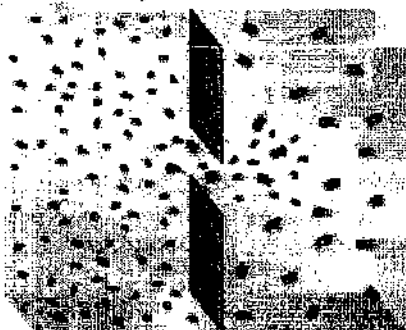
Figure (24) A light molecule diffuses quicker than a heavy molecule

In 1829 Graham formulated what is now known as Graham's Law of Diffusion. It states that:

"Under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses". Mathematically the law can be expressed as

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Where: r_1 and r_2 are the rates of diffusion of gases 1 and 2, while M_1 and M_2 are their molecular masses. When a gas escapes through a pin-hole into a region of low pressure or vacuum, the process is called Effusion. The rate of effusion of a gas also depends, on the molecular mass of the gas.



(a) Diffusion



(b) Effusion

Figure (25) (a) Diffusion is mixing of gas molecules by random motion under conditions where molecular collisions occur. (b) Effusion is escape of a gas through a pinhole without molecular collisions.

Dalton applied a mathematical equation for effusion for the gases which is known as Dalton's law of effusion.

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad (P \text{ \& T constant})$$

$$\therefore \text{The velocity} = \frac{\text{Distance}}{\text{time}}$$

On making a comparison between the velocity of two different gases, it must be measured for the same distance, therefore the velocity of gas diffusion is inversely proportional to the diffusion time (t) (the distance constancy), i.e.:

$$r \propto \frac{1}{t} \quad \Rightarrow \quad \therefore \frac{r_1}{r_2} = \frac{t_2}{t_1}$$

For the same gas and for two different temperatures:

$$r_1 = \sqrt{\frac{3RT_1}{M}} \quad \& \quad r_2 = \sqrt{\frac{3RT_2}{M}}$$

$$\therefore \frac{r_1}{r_2} = \frac{t_2}{t_1} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \frac{\sqrt{T_2}}{\sqrt{T_1}}$$

Whereas r is the velocity of gas diffusion, t is the diffusion time (the effusion time from very little pore), d is the gas density, M is the gas molecular weight and T is the experimental absolute temperature.

Example 29: The effusion time of a certain volume of unknown gas from pin-hole is 112.2 s and the necessary time for effusion of the same volume of oxygen gas is 84.7 s. Find the molecular weight of the unknown gas.

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad \Rightarrow \quad \therefore \frac{112.2 \text{ s}}{84.7 \text{ s}} = \frac{\sqrt{M_x}}{\sqrt{32 \text{ g mol}^{-1}}}$$

$$\therefore \frac{(112.2)^2}{(84.7)^2} = \frac{M_x}{32 \text{ g mol}^{-1}} \quad \Rightarrow \quad \therefore M_x = 56.15 \text{ g mol}^{-1}$$

Example 30: The ratio of velocity of hydrogen gas effusion to another non-inert gas is 3.996. What is the other gas?

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad \Rightarrow \quad \frac{r_{H_2}}{r_x} = \frac{\sqrt{M_x}}{\sqrt{M_{H_2}}}$$

$$\frac{3.996 r_x}{r_x} = \frac{\sqrt{M_x}}{\sqrt{2}} \quad \Rightarrow \quad \sqrt{M_x} = 3.996 \times \sqrt{2}$$

$$M_x = 16 \times 2 = 32 \text{ g mol}^{-1}$$

- ∴ The gas is not inert gas, it is in dual form.
- ∴ The gas is oxygen O_2

Dalton's Law of Partial Pressure:

By using the ideal gas law, we can determine many properties of an individual gas. In many instances, however, we encounter interesting situations with more than one gas present. Our consideration of the levels of pollutants in air is an obvious example. Even if we ignore any pollutants present, clean air is already a mixture of gases. Aside from the possibility of chemical reactions, how do the observed properties of a gas mixture differ from those of pure gases?

The answer to this question is actually suggested by the gas law. In particular, note that none of the terms in the gas law equation depends on the identity of the gas. Consider a sample of air and for simplicity assume that it consists entirely of N_2 and O_2 . Assuming that the air behaves ideally, its pressure can be expressed using the gas law:

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

Here n is the total number of moles of air present. But this total number of moles will simply be the sum of the moles of each component:

$$n_{\text{total}} = n_{N_2} + n_{O_2}$$

We can insert this into the expression above, giving:

$$P = \frac{nRT}{V} = \frac{(n_{N_2} + n_{O_2})RT}{V} = \frac{n_{N_2}RT}{V} + \frac{n_{O_2}RT}{V}$$

Each of those last two nRT/V terms has a special significance; they are the pressures that we would see if only one of the components of the gas mixture were present. If the nitrogen were the only gas present, n_{O_2} would be zero, and we would be left with:

$$P = P_{N_2} = \frac{n_{N_2}RT}{V}$$

If only oxygen were present, we could write a similar result for P_{O_2} . For a mixture, the observed pressure is the sum of the hypothetical partial pressures of the individual gases.

This concept, first established by John Dalton, is sometimes referred to as Dalton's law of partial pressures: *The pressure of a mixture of gases is the sum of the partial pressures of the*

component gases. In simple terms, the partial pressure is what the pressure would be if only that component were present. As long as the component gases behave ideally and do not actually react with one another, this relationship will hold for any gas mixture.

Suppose the presence of a mixture of gases do not react with each others, 1, 2, 3, ... in a certain volume V at constant temperature T , and their quantities are $n_1, n_2, n_3, \dots$. And the total of the gases is n_t . The partial pressures of gases are $P_1, P_2, P_3, \dots$. And the total pressure of the mixture is P_t .

$$\therefore P_t = P_1 + P_2 + P_3 + \dots \quad (1)$$

$$n_t = n_1 + n_2 + n_3 + \dots \quad (2)$$

$$P_1 = \frac{RT}{V} n_1 \quad \& \quad P_2 = \frac{RT}{V} n_2 \quad \& \quad P_3 = \frac{RT}{V} n_3 \quad (3)$$

It is evident from the last equations the the gas pressure is dependent on its quantity (n) only, and is called the partial pressure of the gas.

Taking the summation of the equation (1), we get:

$$P_1 + P_2 + P_3 + \dots = \frac{RT}{V} (n_1 + n_2 + n_3 + \dots) \quad (4)$$

$$P_t = \frac{RT}{V} n_t \quad (5)$$

By dividing equation (3) to equation (5):

$$\frac{P_1}{P_t} = \frac{n_1}{n_t} \quad \& \quad \frac{P_2}{P_t} = \frac{n_2}{n_t} \quad \& \quad \frac{P_3}{P_t} = \frac{n_3}{n_t}$$

i.e.;

$$\frac{P_i}{P_t} = \frac{n_i}{n_t} \quad (6)$$

These expressions suggest another way to understand partial pressures. We might choose to express the concentration of each component gas in terms of its mole fraction, defined as:

$$X_i = \frac{n_i}{n_1 + n_2 + n_3 \dots (n_t)} \quad (7)$$

The total mole fraction of the mixture is equal to one:

$$\therefore P_1 = X_1 P_t \quad \& \quad P_2 = X_2 P_t \quad \& \quad P_3 = X_3 P_t \quad (8)$$

By summation of the last relations in equation (8):

$$P_1 + P_2 + P_3 + \dots = (X_1 + X_2 + X_3 + \dots) P_t$$

$$X_1 + X_2 + X_3 = 1$$

$$\therefore P_1 + P_2 + P_3 + \dots = P_t$$

Figure (17) illustrate Dalton's law of partial pressures of a mixture of gases experimentally. As shown in figure (17 a) There are two separate gases in two flasks connected through a valve, each gas has a partial pressure. Addition of oil through a funnel with

opening the valve to permit the gas to transfe~~r~~ to another flask with the othe~~r~~ gas. It is noticed that the total pressure is the summation of the partial pressure of the two gases as illustrated in figure (17 b).

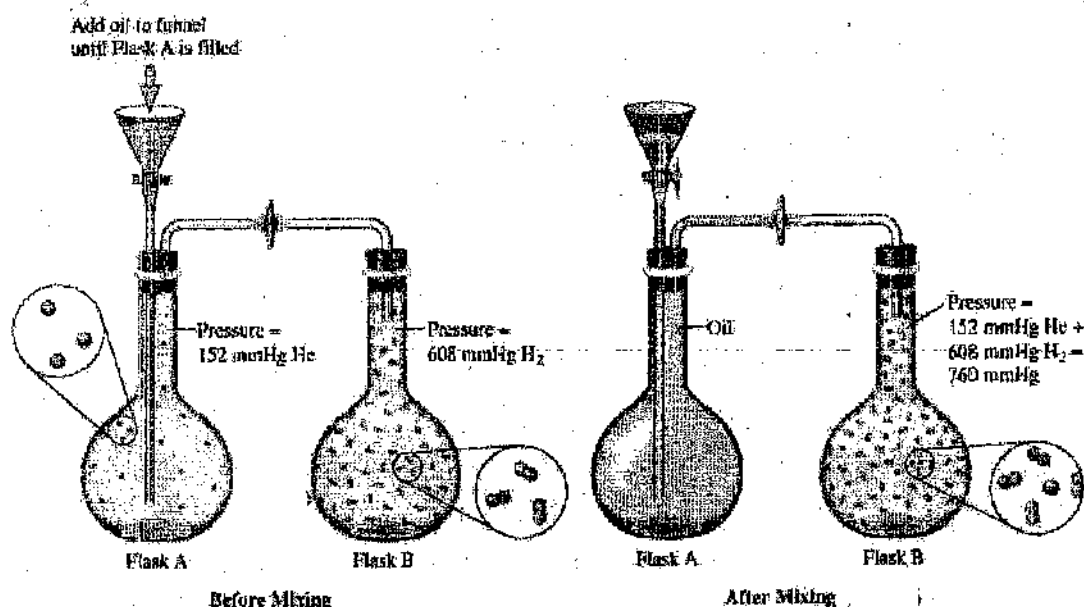


Figure (26) An Experiment to illustrate Dalton's Law of partial pressure of mixture of gases

Example 31: Calculate the partial pressure for both of oxygen and nitrogen gases in a sample of atmosphere air; its pressure is 50 kPa, knowing that the oxygen percentage is 20% in this sample.

$$\therefore X_{O_2} = \frac{1}{5} = 0.2 \quad \& \quad X_{N_2} = \frac{4}{5} = 0.8$$

$$\therefore P_i = X_i \cdot P_{\text{total}}$$

$$\therefore P_{O_2} = X_{O_2} \times P_{\text{total}} = 0.2 \times 50 \text{ kPa} = 10 \text{ kPa}$$

$$\therefore P_{N_2} = X_{N_2} \times P_{\text{total}} = 0.8 \times 50 \text{ kPa} = 40 \text{ kPa}$$

Example 32: A mixture of two gases consists of 40 g oxygen and 40 g helium, its pressure is 0.9 atm. What is the partial pressure of both of the two gases?

$$\therefore n = \frac{w}{M}$$

$$\therefore n_{O_2} = \frac{40 \text{ g}}{32 \text{ g mol}^{-1}} = 1.25 \text{ mol}$$

$$\therefore n_{He} = \frac{40 \text{ g}}{4 \text{ g mol}^{-1}} = 10 \text{ mol}$$

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{He}} = \frac{1.25 \text{ mol}}{(1.25 + 10) \text{ mol}} = 0.111$$

$$X_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{O}_2} + n_{\text{He}}} = \frac{10 \text{ mol}}{(1.25+10) \text{ mol}} = 0.889$$

$$\therefore P_i = X_i \cdot P_{\text{total}}$$

$$P_{\text{O}_2} = X_{\text{O}_2} \times P_{\text{total}} = 0.111 \times 0.9 \text{ atm} = 0.0999 \text{ atm}$$

$$P_{\text{He}} = X_{\text{He}} \times P_{\text{total}} = 0.899 \times 0.9 \text{ atm} = 0.8001 \text{ atm}$$

Example 33: 370 ml of oxygen gas is collected over water surface at temperature 23°C under pressure 0.992 atm. What is the volume of the same volume of dry oxygen at STP? Knowing that the pressure of water vapour at 23°C is 0.0277 atm.

$$\therefore P_{\text{total}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

$$P_{\text{O}_2} = P_t - P_{\text{H}_2\text{O}} = 0.992 - 0.0277 = 0.9643 \text{ atm}$$

$$T_1 = 0.0 + 273 = 273 \text{ K} \quad \& \quad T_2 = 23 + 273 = 296 \text{ K}$$

$$P_1 = 0.9643 \text{ atm} \quad \& \quad P_2 = 1.0 \text{ atm}$$

$$V_1 = 370 \text{ ml} \quad \& \quad V_2 = ?$$

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

$$V_2 = 370 \text{ ml} \times \frac{0.9643 \text{ atm} \times 296 \text{ K}}{1.0 \text{ atm} \times 273 \text{ K}} = 386.85 \text{ ml}$$

Example 34: A magnesium metal is put in quantity of water, on addition of dilute hydrochloric acid; a hydrogen gas is evolved according to the following equation:



The gas was collected over water surface in a container of volume 10 L and the measured pressure is equal to 488.61 torr, knowing that the water vapour pressure at the same temperature is 23.76 torr. Calculate the following:

- (i) The hydrogen gas pressure
- (ii) The quantity of water vapour which is accompanied the collection operation.
- (iii) The experiment temperature.
- (iv) The necessary mass of magnesium to produce 0.5 g hydrogen gas.

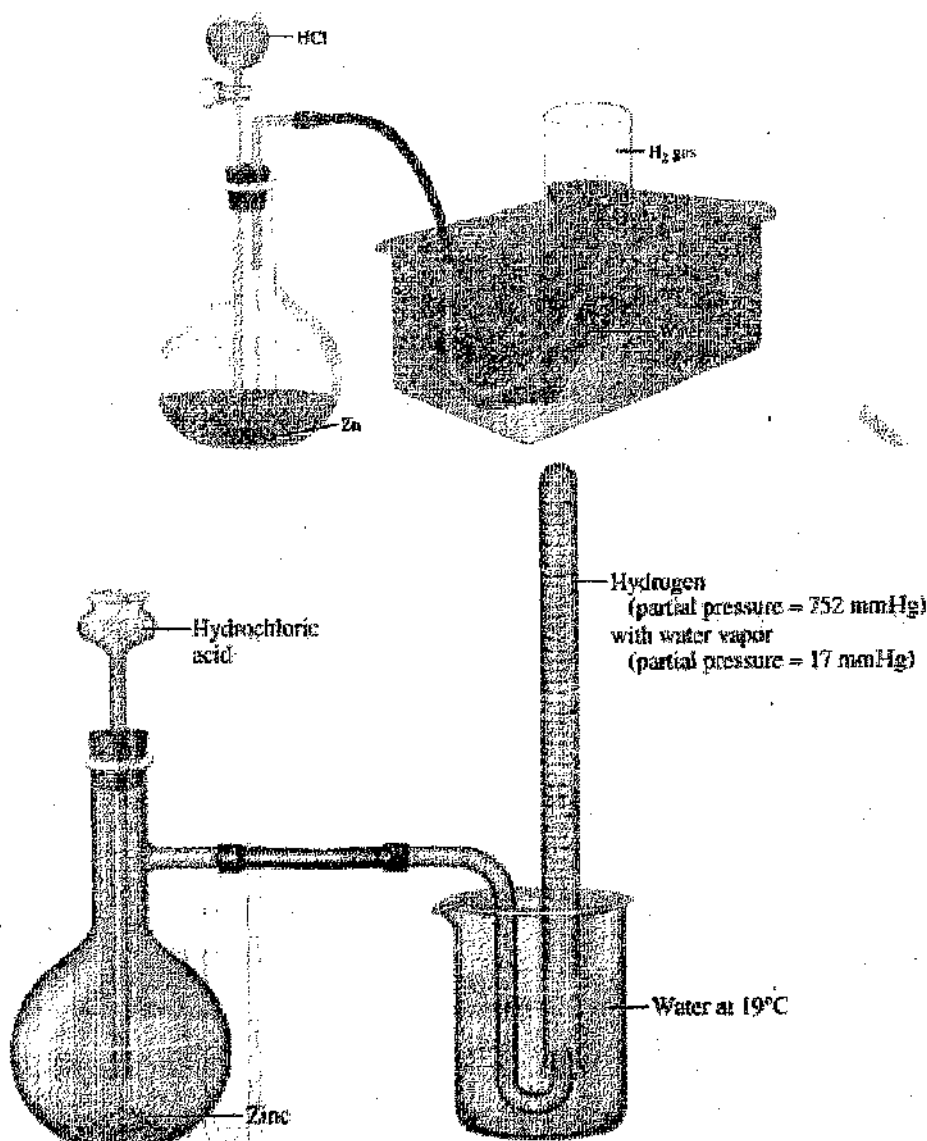


Figure (18) Collection of gas over water: hydrogen gas is prepared by the reaction of zinc with hydrochloric acid. It is led to an inverted tube initially filled with water. When the gas-collection tube is adjusted so that the water level is at the same height as the level in the beaker, the gas pressure in the tube equals the barometric pressure (769 mmHg). The total gas pressure equals the sum of the partial pressure of the hydrogen (752 mmHg) and the vapour pressure of water 917 mmHg. For clarity, hydrochloric acid is shown in the light and hydrogen gas in light blue.

$$\begin{aligned}
 \text{(i)} \quad & P_{\text{total}} = P_{\text{H}_2} + P_{\text{H}_2\text{O}} \\
 P_{\text{H}_2} &= P_t - P_{\text{H}_2\text{O}} = 488.61 - 23.76 = 464.85 \text{ torr} \\
 \therefore P_{\text{H}_2} &= X_{\text{H}_2} \cdot P_{\text{total}} \\
 \therefore X_{\text{H}_2} &= \frac{P_{\text{H}_2}}{P_{\text{total}}} = \frac{464.85 \text{ torr}}{488.61 \text{ torr}} = 0.951
 \end{aligned}$$

$$n_{H_2} = \frac{w_{H_2}}{M_{H_2}} = \frac{0.5 \text{ g}}{2 \text{ g mol}^{-1}} = 0.25 \text{ mol}$$

$$X_{H_2} = \frac{n_{H_2}}{n_{\text{total}}}$$

$$n_{\text{total}} = \frac{n_{H_2}}{X_{H_2}} = \frac{0.25 \text{ mol}}{0.951} = 0.263 \text{ mol}$$

$$(ii) \quad n_{\text{total}} = n_{H_2} + n_{H_2O} = 0.263 \text{ mol}$$

$$n_{H_2O} = n_{\text{total}} - n_{H_2} = 0.263 - 0.25 = 0.013 \text{ mol}$$

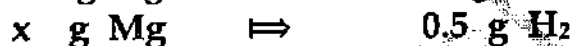
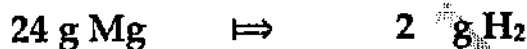
$$(iii) \quad \therefore P_t V = n_t RT$$

$$T = \frac{P_t \cdot V}{n_t \cdot R} = \frac{\frac{488.61 \text{ torr}}{760 \text{ torr}} \text{ atm} \times 10 \text{ L}}{0.263 \text{ mol} \times 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}} = 298 \text{ K}$$

$$T \text{ K} = t \text{ } ^\circ\text{C} + 273$$

$$t \text{ } ^\circ\text{C} = T \text{ K} - 273 = 298 - 273 = 25^\circ\text{C}$$

(iv)



$$\therefore x \text{ g Mg} = \frac{24 \text{ g Mg} \times 0.5 \text{ g H}_2}{2 \text{ g H}_2} = 6 \text{ g}$$

$\therefore$ The necessary magnesium metal weight is 6 g

Student Exercises

- 1- What is the difference between: (i) Air (ii) atmosphere
- 2- Shall increasing the temperature of quantity of gas from 100°C to 200°C at constant pressure the volume will be duplicated? Why?
- 3- The temperature of quantity of gas at constant pressure is changed from 100°C to 200 K. Shall the gas volume is increased and why?
- 4- Shall the increasing the temperature of quantity of gas from 100°C to 200°C at constant volume the pressure will be duplicated? why?
- 5- The temperature of quantity of gas at constant volume is changed from 100°C to 200 K. Shall the gas pressure is increased and why?
- 6- A sample of gas under pressure 0.814 atm in container 300 cm^3 at temperature 20°C . What is the pressure for the same quantity of gas in container 500 cm^3 at temperature 50°C ?
- 7- It was found that the pressure of certain quantity of gas in container its volume is 4 L under pressure 3 atm and temperature

30°C. The gas is compressed to 1.5 atm in container. its volume 7.5 L. What will be the temperature in this case?

8- What is meant by the molar volume for a gas? What is its value at standard conditions (STP)?

9- Deduce the relation between the gas density and its molar weight.

10- If you have equal masses of oxygen gas O_2 , hydrogen gas H_2 and methane gas CH_4 at the same conditions of temperature and pressure. Calculate the ratio between their volumes.

12- What is the density of a gas its effusion velocity is 1.414 times of effusion velocity of sulphur dioxide gas (SO_2) at standard conditions?

13- Compare between the velocity of effusion of hydrogen gas at 10°C and at 90°C.

14- Gas A is effused through a pin-hole with time 1.44 min, and at the conditions of pressure and temperature, the same volume of oxygen gas is effused in time 1.8 min. What is the density of gas A and its molecular weight?

15- You have two gases, hydrogen bromide (HBr) and methane gas (CH_4), the hydrogen bromide is effused through pin-hole with rate 4 ml/s. What is the rate of leakage rate of methane gas through the same pore?

16- Calculate the molecular weight of a gas its rate of effusion is 4.69 times the effusion rate of carbon dioxide (CO_2).

17- If the rate of effusion of unknown gas is a half of the rate of effusion of oxygen gas. What is the molecular weight of the unknown gas?

18- 50 ml of gas (A) is effused through a pin-hole in 146 s while the same volume of carbon dioxide gas (CO_2) is effused through the same pin-hole at the same conditions of pressure and temperature in 115 s. Calculate the molecular weight of the gas (A).

19- A 0.1 mole of an ideal gas was collected over the water in a container of volume 2.5 L till the pressure 645 is reached. If you know that the effusion velocity of the gas is equal to 83.5% of the effusion velocity of nitrogen gas (N_2) at the same conditions of pressure and temperature, find the molecular weight of the gas.

20- The density of nitrogen gas (N_2) is 0.572 g/L at temperature 25°C and pressure 0.5 atm and the rate of diffusion of the nitrogen gas is 9.5 ml/s. What is the density of a certain sample of gas

which is diffuses with rate 6.28 ml/s through the same pore and at the same conditions of temperature and pressure and what is its molecular weight?

21- Compare between the density and diffusion rate for both of hydrogen and oxygen gases at the same conditions of pressure and temperature.

22- A mixture of two gases consists of 2 g of hydrogen gas (H_2) and 8 g of oxygen gas (O_2). Compare between the following at the same conditions of pressure and temperature:

i) Their volumes (ii) Their diffusion rates (iii) Their densities

23- A mixture of two gases consists of 2 g of helium gas (He) and 16 g of sulphur dioxide gas (SO_2). Compare between the following at the same conditions of pressure and temperature:

i) Their volumes (ii) Their diffusion rates (iii) Their densities

24- The pressure of quantity of nitrogen gas in a container its volume is 1.0 L is 2.0 atm at temperature $20^\circ C$ while the pressure of another quantity of oxygen gas in container its volume is 5.0 L under pressure 1.5 atm and temperature $23^\circ C$. The two quantities are collected in a container its volume is 10 L. How much will be the total pressure of the mixture in this container at temperature $25^\circ C$?

25- Flask has a capacity of 2000 cm^3 contains n mole of nitrogen gas (N_2) under pressure 36 cmHg and temperature $T\text{ K}$. At addition of 0.32 g of oxygen gas (O_2), it was necessary to lower the temperature to $10^\circ C$, in order to get the same last pressure. Calculate both of temperature (T) and number of moles (n).

26- Flask has a capacity of 2.0 L contains (n) mole of nitrogen gas (N_2) under pressure 0.5 atm and temperature $T\text{ K}$. At addition of 0.01 mole of nitrogen gas (N_2), it was necessary to lower the temperature to $10^\circ C$, in order to get the same last pressure. Calculate both of temperature (T) and number of moles (n).

27- A gas mixture has equal grams of ethane gas (C_2H_6) and carbondioxide (CO_2), the partial pressure of ethane gas is 22 mmHg. What is the partial pressure of carbon dioxide gas?

28- The partial pressure of methane gas (CH_4) is 0.225 atm and for ethane gas (C_2H_6) is 0.165 atm in a mixture of them.

i) What is the mole fraction for each gas in the mixture?

ii) If the mixture occupies a volume 9.73 L at temperature $35^\circ C$. What is the total number of mixture moles?

iii) How many grams of each gas in the mixture?

29- A sample of nitrogen gas (N_2) is collected using the electrolysis method of water, its volume 152 cm^3 at temperature 25°C under pressure 758 mmHg . If you know that the vapour pressure of water at the same temperature is 23.76 mmHg . Calculate:

- The partial pressure of hydrogen gas.
- The number of moles of hydrogen gas produced.
- The mole fraction for both hydrogen and water vapour in gas mixture.

30- Arrange the following gases according to their velocity of diffusion. Compare between the diffusion velocity of the faster one and the slower one at the same conditions: (He , H_2 , Ar , NH_3 , CO_2 , SO_2).

31- Out of the following pairs of gases, which will diffuse through a porous plug with the same diffusion rate?

- (a) NO , CO (b) CH_4 , O_2 (c) NO_2 , CO_2 (d) NO , C_2H_6

32- The pressure of a gas mixture of two equal weights, its summation is 1.12 g of oxygen and nitrogen gases is 0.6 atm . What is the partial pressure of every gas?

33- The pressure of a mixture of two equal weights of gases is 2.24 g of helium and nitrogen gas is 0.7 atm . Calculate the partial pressure of each gas.

34- The pressure of a certain quantity of gas is 450 torr in a container 200 cm^3 at 300 K . How much its pressure will be at the same temperature if:

- (i) Its quantity is doubled. (ii) The gas is transferred to another container its volume is 300 cm^3 . (iii) Find the original gas quantity.

35- 14 g of nitrogen gas are put with 16 g of oxygen gas in a container; its volume is 10 L at room temperature. Shall their partial pressure are equal and why? What is the total pressure of the mixture?

36- A 10 liter vessel contained 14 g of nitrogen gas (N_2), 0.4 g hydrogen gas (H_2) and 8 g of oxygen gas (O_2) and at temperature 27°C . What is the total pressure of the vessel?

37- Consider the composite system, which is held at 298 K , shown in the following Figure, assuming ideal gas behavior; calculate the total pressure and the partial pressure of each component by bar units, if the barriers separating the compartments are removed. Assume that the volume of the barriers is negligible.



He
2.0 L
1.50 bar

Ne
3.00 L
2.50 bar

Xe
1.00 L
1.00 bar

38- Why real gas deviates from the ideal gas behaviour - write the equation which expresses the behaviour of real gas and ideal gas - which circumstances can be the real gas behaves ideally and why?

MULTIPLE CHOICE QUESTIONS

1- According to Boyle's law the volume of a fixed mass of a gas, at constant temperature, is:

- (a) directly proportional to its pressure
- (b) inversely proportional to its pressure
- (c) the square root of its pressure
- (d) none of these

Answer: (b)

2- Mathematically, Boyle's law can be represented as

- (a) $V \propto \frac{1}{P}$
- (b) $V = \frac{k}{P}$
- (c) $VP = k$
- (d) all of these

Answer: (d)

3- At constant temperature, the pressure of the gas is reduced to one third, the volume

- (a) reduces to one third
- (b) increases by three times
- (c) remains the same
- (d) cannot be predicted

Answer: (b)

4- At constant pressure, the volume of a fixed mass of a gas is

- (a) directly proportional to its temperature
- (b) directly proportional to its absolute temperature
- (c) inversely proportional to its temperature
- (d) inversely proportional to its absolute temperature

Answer: (b)

5- Which of the following is the correct mathematical relation for Charles's law at constant pressure?

- (a) $V \propto T$
- (b) $V \propto t$
- (c) $V = kt$
- (d) none of these

Answer: (a)

6- According to Gay Lussac's law for a fixed volume of a given gas

- (a) $\frac{P}{T} = \text{a constant}$
- (b) $P \propto \frac{1}{T}$
- (c) $P = \frac{k}{T}$
- (d) $PT = k$

Answer: (a)

7- "Equal volume of all gases at the same temperature and pressure contain equal number of molecules" is the statement of:

- (a) combined gas law (b) Charle's law
(c) Avogadro's law (d) Boyle's law

Answer: (c)

8- For one mole of a gas, the ideal gas equation is

- (a) $PV = RT$ (b) $PV = \frac{1}{2}RT$ (c) $PV = \frac{3}{2}RT$ (d) $PV = \frac{5}{2}RT$

Answer: (a)

9- The units of R, the gas constant are

- (a) $\text{erg K}^{-1} \text{mol}^{-1}$ (b) $\text{cal K}^{-1} \text{mol}^{-1}$
(c) $\text{joule K}^{-1} \text{mol}^{-1}$ (d) all of these

Answer: (d)

10- In $\text{lit atm K}^{-1} \text{mol}^{-1}$ the numerical value of R, the gas constant, is

- (a) 0.821 (b) 0.0821 (c) 0.00821 (d) 0.000821

Answer: (b)

11- "The total pressure of a mixture of gases (non-reacting) is equal to the sum of the partial pressures of all the gases present" is the statement of:

- (a) Graham's law of diffusion (b) Dalton's law of partial pressures
(c) Avogadro's law of partial pressures (d) none of these

Answer: (b)

12- Under same conditions of temperature and pressure, the rates of diffusion of different gases are

- (a) directly proportional to the square roots of the molecular masses
(b) directly proportional to the square roots of their vapour densities
(c) inversely proportional to the square roots of their molecular masses
(d) inversely proportional to the square roots of their molar volumes

Answer: (c)

13- The average kinetic energy of the gas molecules is

- (a) inversely proportional to its absolute temperature
(b) directly proportional to its absolute temperature
(c) equal to the square of its absolute temperature
(d) directly proportional to the square root of its absolute temperature

Answer: (b)

14- For one mole of a gas the kinetic energy is given by

- (a) $E = \frac{1}{2}RT$ (b) $E = \frac{3}{2}RT$ (c) $E = \frac{5}{2}RT$ (d) $E = \frac{7}{2}RT$

Answer: (b)

15- The kinetic gas equation is given by the relation

- (a) $PV = \frac{1}{2} m N \mu^2$ (b) $PV = \frac{1}{3} m N \mu^2$
(c) $PV = \frac{3}{2} m N \mu^2$ (d) $PV = \frac{2}{3} m N \mu^2$

Answer: (a)

16- The average velocity of a gas is given by

- (a) $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$ (b) $\bar{v} = \sqrt{\frac{3RT}{\pi M}}$ (c) $\bar{v} = \sqrt{\frac{2RT}{\pi M}}$ (d) $\bar{v} = \sqrt{\frac{RT}{\pi M}}$

Answer: (a)

17- The root mean square velocity of gas molecules is given by the relation

(a) $\mu = \sqrt{\frac{RT}{M}}$ (b) $\mu = \sqrt{\frac{2RT}{M}}$ (c) $\mu = \sqrt{\frac{3RT}{M}}$ (d) $\mu = \sqrt{\frac{8RT}{M}}$

Answer: (c)

18- The root mean square velocity gas molecules is given by the relation

(a) $\mu = \sqrt{\frac{3PV}{M}}$ (b) $\mu = \sqrt{\frac{3RT}{M}}$ (c) $\mu = \sqrt{\frac{3P}{D}}$ (d) all o these

Answer: (d)

19- The free path is the distance travelled by the molecule

- (a) before collision (b) in one second
(c) after collision (d) in one minute

Answer: (a)

20- The mean free path is

- (a) directly proportional to the pressure of the gas
(b) directly proportional to the root mean square velocity of gas
(c) directly proportional to the temperature of the gas
(d) directly proportional to the absolute temperature of the gas

Answer: (d)

21- The collision frequency of a gas is

- (a) directly proportional to the square root of absolute temperature
(b) directly proportional to the absolute temperature
(c) inversely proportional to the pressure of the gas
(d) inversely proportional to the absolute temperature

Answer: (b)

22- The value of γ , the specific heat ratio, for a monoatomic gas is

- (a) 0.0 (b) 1.40 (c) 1.667 (d) 1.33

Answer: (a)

23- The compressibility factor, z i.e. the extent to which a real gas deviates from ideal behaviour is given by

(a) $z = \frac{PV}{RT^2}$ (b) $z = \frac{PV}{2RT}$ (c) $z = \frac{PV}{RT}$ (d) $z = \frac{2PV}{RT}$

Answer: (c)

24- The real gases show nearly ideal behaviour at

- (a) low pressures and low temperatures
(b) high pressures and low temperatures
(c) high pressures and high temperatures
(d) low pressures and high temperatures

Answer: (d)

25- Excluded volume is _____ times the actual volume of molecules.

- (a) $\frac{1}{2}$ (b) two (c) three (d) four

Answer: (d)

26- The pressure P in the ideal gas equation is replaced by

(a) $\left(P + \frac{an^2}{V^2}\right)$ (b) $\left(P - \frac{an^2}{V^2}\right)$ (c) $\left(P + \frac{2n^2}{V^2}\right)$ (d) $\left(P + \frac{n^2}{2V^2}\right)$

Answer: (a)

27- The units of 'a' the van der Waal's constant are

- (a) atm L mol^{-1} (b) $\text{atm L}^{-1} \text{mol}^{-1}$
(c) $\text{atm L}^{-2} \text{mol}^{-2}$ (d) $\text{atm L}^{-1} \text{mol}^{-2}$

Answer: (c)

28- Which one of the following relations is correct?

- (a) $V_c = 3b$ (b) $P_c = \frac{a}{27 R b^2}$ (c) $T_c = \frac{8a}{27 R b}$ (d) none of these

Answer: (d)

29- How many molecules are present in 0.2 g of hydrogen?

- (a) 6.023×10^{23} (b) 6.023×10^{22} (c) 3.0125×10^{23} (d) 3.0125×10^{22}

Answer: (b)

30- Gas A diffuses twice as fast as another gas B. If the vapour density of the gas A is 2, the molecular mass of gas B is:

- (a) 2 (b) 4 (c) 8 (d) 16

Answer: (d)

31- A container contains a gas at 1 atm pressure. To compress it to $\frac{1}{3}$ rd of its initial volume, pressure to be applied is

- (a) 1 atm (b) 2 atm (c) 3 atm (d) 6 atm

Answer: (c)

32- The ratio of most probable velocity, average velocity and root-mean square velocity of molecules of a gas is

- (a) 1 : 1.128 : 1.224 (b) 1.128 : 1 : 1.224
(c) 1.128 : 1.224 : 1 (d) 1.224 : 1 : 1.128

Answer: (a)

33- Which of the following gases will have the highest rate of diffusion?

- (a) CH_4 (b) NH_3 (c) N_2 (d) CO_2

Answer: (a)

34- 290 ml of a gas at 17°C is cooled to -13°C at constant pressure. The new volume of the gas will be:

- (a) 260 ml (b) 270 ml (c) 280 ml (d) 290 ml

Answer: (a)

35- The volume of a gas at 0°C is 273 mL. Its volume at 12°C and the same pressure will be:

- (a) $273 + \frac{12}{273} \text{ mL}$ (b) $273 + \frac{273}{12} \text{ mL}$ (c) $273 + 12 \text{ mL}$ (d) $273 - 12 \text{ mL}$

Answer: (c)

36- If the pressure and absolute temperature of 3 litres of a gas are doubled, its volume would be:

- (a) 2 litres (b) 3 litres (c) 6 litres (d) 12 litres

Answer: (b)

37- The root-mean square velocity of a certain gas at 27°C is $y \text{ cm s}^{-1}$. The temperature at which its velocity will be $2y$ is:

- (a) 54°C (b) 108°C (c) 600 K (d) 1200 K

Answer: (d)

38- Out of the following pairs of gases, which will diffuse through a porous plug with the same rate of diffusion?

- (a) NO , CO (b) CH_4 , O_2 (c) NO_2 , CO_2 (d) NO , C_2H_6

Answer: (d)

39- 8 g of CH_4 and 2 g of hydrogen are mixed and kept at 760 mm pressure at 273 K. The total volume occupied by the mixture will be:

- (a) 11.2 litres (b) 22.4 litres (c) 33.6 litres (d) 44.8 litres

Answer: (c)

40- The root-mean square velocity of a certain gas at 27°C is $am \text{ s}^{-1}$. Its root-mean square velocity at 927°C is

- (a) $\frac{a}{2} \text{ m s}^{-1}$ (b) $2a \text{ m s}^{-1}$ (c) $3a \text{ m s}^{-1}$ (d) $6a \text{ m s}^{-1}$

Answer: (b)

41- In a closed flask of one litre, 2.0 g of hydrogen gas is heated from 27°C to 327°C. Which of the following is incorrect?

- (a) the pressure of the gas increases
(b) the kinetic energy of gaseous molecules increases
(c) the rate of collision increases
(d) the number of moles of the gas increases

Answer: (d)

42- Which of the following gases will have the lowest rate of diffusion?

- (a) H_2 (b) N_2 (c) F_2 (d) O_2

Answer: (c)

43- A gas is heated at constant temperature. Then:

- (a) the no. of molecules of the gas increases
(b) the kinetic energy of the gas molecules decreases
(c) the kinetic energy of the gas molecules remains unaltered
(d) the kinetic energy of the gas molecules increases

Answer: (c)

44- Equal volumes of methane and ethane are mixed in an empty container at 25°C. The fraction of total pressure exerted by ethane is:

- (a) $\frac{1}{2}$ (b) $\frac{2}{3}$ (c) $\frac{8}{15}$ (d) $\frac{3}{2}$

Answer: (a)

45- In van der Waal's equation of state for a non-ideal gas the net force of attraction among the molecules is given by:

- (a) $\frac{a n^2}{V^2}$ (b) $P + \frac{a n^2}{V^2}$ (c) $P - \frac{a n^2}{V^2}$ (d) $-\frac{a n^2}{V^2}$

Answer: (a)

46- The compressibility factor, z , for an ideal gas is

- (a) zero (b) less than one
(c) greater than one (d) equal to one

Answer: (d)

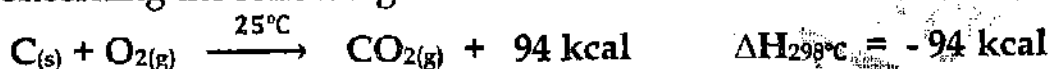
Thermochemistry

It is noticed that energy in the form of heat (thermal energy) is generally evolved or absorbed as a result of a chemical change.

Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

Thermochemistry is concerned with the heat that accompanies chemical reactions. Thermochemical data are usually expressed by writing the equation for the chemical reaction and giving the value of the enthalpy change (ΔH) after the reaction.

Concerning the following reaction:



Which implies that when 12 g of solid carbon (C) reacts with 32 g of oxygen gas (O_2) at constant pressure and temperature an amount of heat (equivalent to 94 kcal), is produced? In other words the increase of the heat content of this reaction is $\Delta H = -94$ kcal, at temperature 25°C .

The enthalpy change (ΔH) is also called the heat of reaction and it is the difference between the heat content of the resultant and reactants at constant pressure and temperature, if ΔH is negative as in the above equation, the heat content of the resultants are less than the heat content of the reactants, i.e.; carbon and oxygen are in high energy level than carbon dioxide gas (CO_2). This reaction is described as "exothermic reaction" in character. Most reactions are taking place at ordinary temperature are exothermic, and exothermic compounds, i.e.; their formation is accompanied by evolution of heat are stable at ordinary temperature and they decompose only at higher temperatures. Endothermic compounds, on the other hand, are stable only at higher temperatures and decompose at ordinary temperature.

Heat of reaction depends on the state under which the reaction taking place according to:

(i) Heat of the reaction under constant volume, ΔE :

It is the amount of heat evolved or absorbed when the reaction taking place under constant volume. In this case the heat evolved or absorbed is on the expense of the internal energy of the system:

$$\Delta E = E_{\text{resultant}} - E_{\text{reactants}}$$

Where: E is the internal energy.

(ii) Heat of reaction under constant pressure, ΔH :

If the system is allowed to expand during the reaction, it does work against the atmosphere and extra heat is evolved or absorbed in doing this work. Therefore ΔH differs from ΔE by the amount of work done.

Relation between ΔH and ΔE :

$$\Delta H = \Delta E + w \quad (1)$$

Where w is the work done, when the system expands against a constant pressure, P .

$$\text{The work done } (w) = P\Delta V \quad (2)$$

Where ΔV is the change in volume.

If the products and reactants have the same volume ΔH is the same as ΔE .

Notice that equation (1) the work may be negative or positive sign according to the system is doing work on the surrounding or vice versa. If the the sydtem has done work on the surrounding, the the work has a negative sign because the the system has lost energy and vice versa.

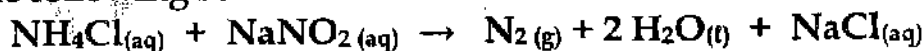
It is clear the the work units is energy units (Joule) in international units system, which is called units (SI). The units of exerted work are the effective force by one Neuton through a one meter distance. Also, the wrk can be expressed with other units such as erg or calorie etc. The relation between these units is given as following:

$$1.0 \times 10^7 \text{ erg} = 1.0 \text{ Joule}$$

$$1.0 \text{ calorie} = 4.184 \text{ Joule}$$

$$1.0 \text{ Liter atmosphere (L atm)} = 101.39 \text{ Joule}$$

Example 1: If the change in internal enrgy under constant volume for the following reaction:



Is equal to (- 333 kJ) when one mole of nitrogen gas is produced. If the production of one mole of nitrogen gas is making the volume system to be increased by 22.4 L at pressure 1.0 atm, calculate the heat of reaction with joule units at constant pressure.

Solution:

$$P\Delta V = (22.4 \text{ L}) \cdot (1.0 \text{ atm}) = 22.4 \text{ L atm}$$

$$P\Delta V = 22.4 \text{ L atm} \times \frac{101.39 \text{ J}}{\text{L atm}} = 2.27 \times 10^3 \text{ J} = 2.27 \text{ kJ}$$

Applying the relation: $\Delta H = \Delta E + P\Delta V$

$$\Delta H = \Delta E + P\Delta V = -333 \text{ kJ} + 2.27 \text{ kJ} = -330 \text{ kJ}$$

Example 2: The first law of thermodynamic can be represented as following formulas:

(i) $\Delta E = q - w$

(ii) $\Delta E = q + w$

Which conditions for using these two formulas?

Solution:

(i) Can be used if the surrounding is doing work on the system, i.e.; the system acquired energy.

(ii) Can be used if the system is doing work on the surrounding, i.e.; the system loses energy.

(5) From the following three sentences, illustrate which is correct (✓) or false (✗) when the gas is escaping reversibly and isothermally against space with illustrating the reasons: (3 marks)

(ii) $w = P\Delta V + V\Delta P$ (...) (...) (....)

(iii) $w = P\Delta V$ (...); $\Delta E = 0.0$ (...); $q = -P\Delta V$ (...) (....)

(v) $w = 0.0$ (...); $q = 0.0$ (...); $\Delta E = 0.0$ (...) (....)

(iv) $w = 0.0$ (...); $\Delta E = q = +ve$ (...) (....)

(v) $q = -w = +ve$ (...); $\Delta E = 0.0$ (...) (....)

Solution:

∴ The process is isothermal ∴ $\Delta T = 0.0$ ∴ $\Delta E = 0.0$

∴ The gas escape against space ∴ $P = 0.0$

∴ $w = -P\Delta V = 0.0$

From the mathematical expression of first law of thermodynamic:

$\Delta E = q + w$

∴ $q = 0.0$

(i) $w = P\Delta V + V\Delta P$ (✗) (✗)

(ii) $w = P\Delta V$ (✓); $\Delta E = 0.0$ (✓); $q = -P\Delta V$ (✗) (✗)

(iii) $w = 0.0$ (✓); $q = 0.0$ (✓); $\Delta E = 0.0$ (✓) (✓)

(iv) $w = 0.0$ (✓); $\Delta E = q = +ve$ (✗) (✗)

(v) $q = -w = +ve$ (✗); $\Delta E = 0.0$ (✓) (✗)

Example 3: If you have the following processes occurring at constant pressure:

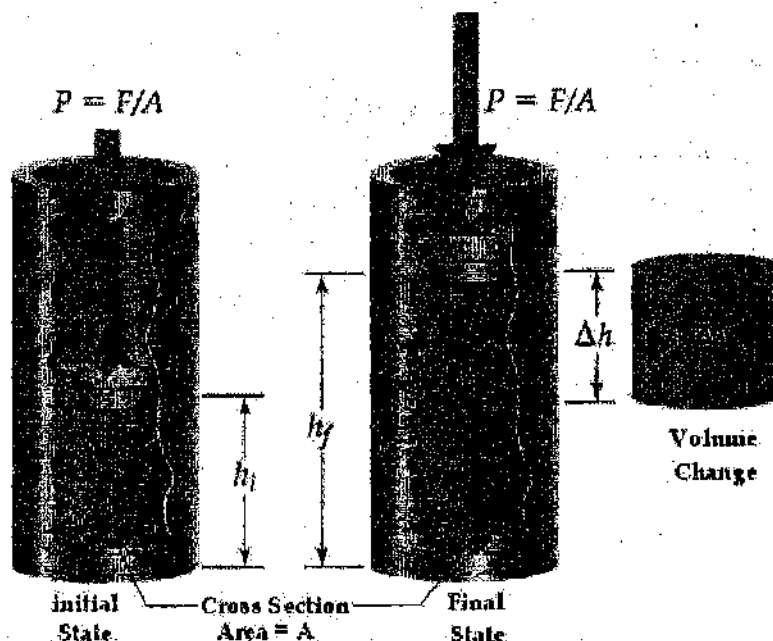
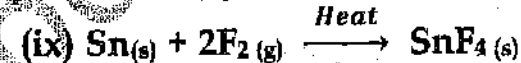
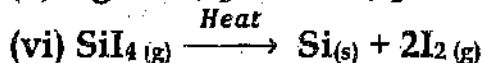
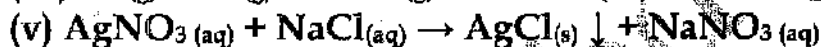
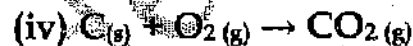
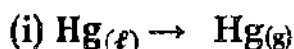


Figure (1) Pressure Volume Work



Illustrate which of these processes, the system is doing work on the surrounding or vice versa or there is no work at all.

Solution:



System on surrounding



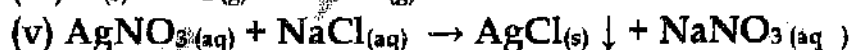
Surrounding on system



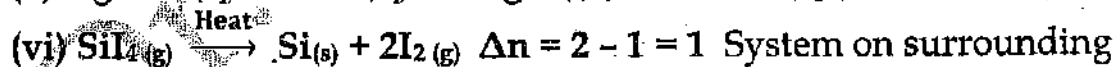
No work



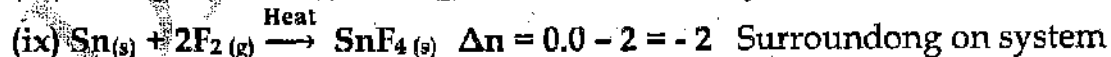
No work



No work



System on surrounding



Surrounding on system

Example 4: As a result of addition an acid to a metal, 30 liters of hydrogen gas is evolved. Calculate the exerted work of the gas with kilo joule unites to overcome the applied standard atmosphere (1.0 atm), assuming temperature constancy.

Solution:

∵ where the atmospheric pressure is constant.

∴ The gas expansion is against this pressure

$$w = -P(V_2 - V_1) = -1 \text{ atm} \times (30 - 0.0) \text{ L}$$

$$w = - 30 \text{ L atm} \times \frac{101.30 \text{ Joules}}{\text{L atm}} = - 3041.7 \text{ J}$$

$$w = - 3.0417 \text{ kJ}$$

Example 5: If the gas is expanded at temperature 25°C from the volume "2 L" to the volume "5L" at constant pressure. Calculate the exerted work with joules when the gas is expanded:

- (i) Against the space (ii) Against pressure equal to 3.0 atm.

Solution:

- (i) ∵ whereas the the gas expansion is against space

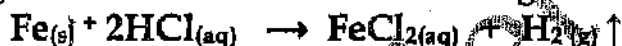
$$\therefore P = 0.0$$

$$\text{The work done (w)} = P\Delta V = 0.0 \times \Delta V = 0.0$$

- (ii) $w = P\Delta V$ & $\Delta V = (5\text{L} - 3\text{L}) 2 \text{ L}$

$$w = - 9 \text{ L atm} \times \frac{101.30 \text{ Joules}}{\text{L atm}} = - 912.51 \text{ J}$$

Example 6: Calculate the exerted work when 50 g of iron is dissolved in hydrochloric acid as the following reaction:



- (i) In closed container

- (ii) In open container

Solution:

From the equation, it is clear that one mole of hydrogen gas is liberated for every consumed one gram mole of iron. The gas is doing work on the surrounding, i.e., the work has a negative sign (-). Assuming ideal gas behaviour and neglecting the initial system volume, we get the following:

$$P\Delta V \approx PV_{(g)} = nRT$$

- (i) In closed container:

$$\therefore \Delta V = 0.0$$

$$\therefore \text{work done (w)} = P\Delta V = P \times 0.0 = 0.0$$

- (ii) In open container

$$w = - P\Delta V = - n_{\text{H}_2} RT$$

$$w = - \frac{50 \text{ g}}{56 \text{ g mol}^{-1}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}$$

$$w = - 0.893 \times 8.314 \text{ J} \times 298 = - 2.212 \text{ kJ}$$

∴ This work does not represent the quantity of maximum exerted work because the expansion against external pressure is constant (irreversible process).

Since, liquids and solids occupy very small volumes; the term $P\Delta V$ for them is considered equal to zero. Therefore, the term $P\Delta V$ is only used in the case of gases. By applying the universal gas equation:

$$PV = nRT \quad (3)$$

and

$$P(V + \Delta V) = (n + \Delta n) RT \quad (4)$$

$$\therefore P\Delta V = \Delta nRT \quad (5)$$

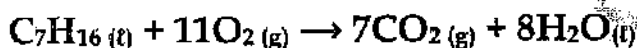
Where, Δn is the change in number of moles of the resulting and reacting gases only.

$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}}$$

Therefore:

$$\Delta H = \Delta E + \Delta nRT \quad (6)$$

Example 7: The heat of combustion of n-heptane at constant volume at temperature 25°C is 1148.93 kcal, according to the following equation:



What is the value of reaction heat under constant pressure?

Solution:

$$R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$$

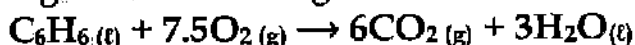
$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}} = 7 - 11 = -4 \text{ mol}$$

$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$\Delta H = -1148.93 \text{ kcal} \times \frac{4.184 \text{ kJ}}{\text{kcal}} - \frac{4 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{\frac{1000 \text{ J}}{\text{kJ}}}$$

$$\Delta H = -4807 \text{ kJ} - 9.910.2 \text{ kJ} = -4816.9 \text{ kJ}$$

Example 8: The accompanied heat of combustion for one mole of benzene at constant volume and temperature (298 K) is equal to -3264.3 kJ. Calculate ΔH for the benzene combustion in presence of oxygen according to the following equation:



What is the value of reaction heat under constant pressure?

Solution:

$$\Delta E = -3264.3 \text{ kJ}$$

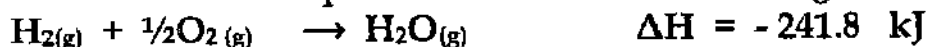
$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}} = 6 - 7.5 = -1.5 \text{ mol}$$

$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$\Delta H = -3264.3 \text{ kJ} - \frac{1.5 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{\frac{1000 \text{ J}}{\text{kJ}}}$$

$$\Delta H = -3264.3 \text{ kJ} - 3.71636 \text{ kJ} = -3268.02 \text{ kJ}$$

Example 9: Calculate the heat of combustion of hydrogen gas at constant volume at temperature 27°C for the following reaction:



Solution:

$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}} = 1 - 1.5 = -0.5 \text{ mol}$$

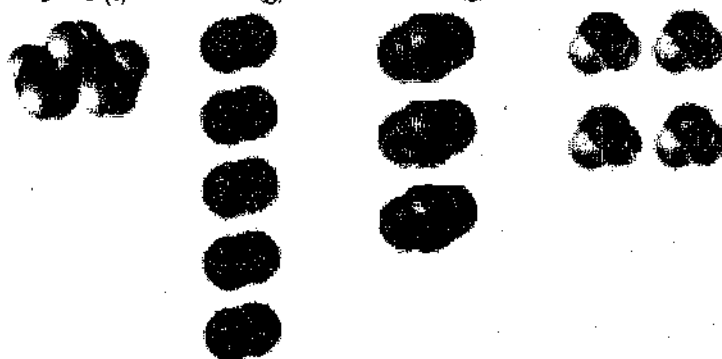
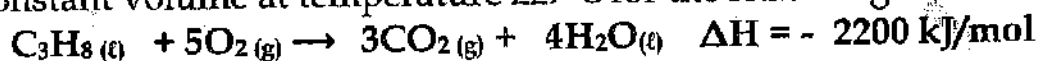
$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$-241.8 \text{ kJ} = \Delta E - \frac{0.5 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{\frac{1000 \text{ J}}{\text{kJ}}}$$

$$-241.8 \text{ kJ} = \Delta E - 1.2471 \text{ kJ}$$

$$\Delta E = -241.8 \text{ kJ} + 1.2471 \text{ kJ} = -240.5529 \text{ kJ}$$

Example 10: Calculate the heat of combustion of hydrogen gas at constant volume at temperature 227°C for the following reaction:



Solution:

$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}} = 3 - (5 + 1) = -3 \text{ mol}$$

$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$-2200 \text{ kJ} = \Delta E - \frac{3 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K}}{\frac{1000 \text{ J}}{\text{kJ}}}$$

$$-2200 \text{ kJ} = \Delta E - 12.471 \text{ kJ}$$

$$\Delta E = -2200 \text{ kJ} + 12.471 \text{ kJ} = -2187.529 \text{ kJ}$$

Example 11: Calculate the excreted work with joule units when the gas volume is increased by "1 cm³" under pressure 1 atm.

Solution:

$$w = -P\Delta V = -1 \text{ atm} \times \frac{1 \text{ cm}^3 \times 1 \text{ L}}{1000 \text{ cm}^3} \times \frac{101.39 \text{ J}}{\text{L atm}} = -0.10139 \text{ J}$$

Example 12: Calculate the excreted work with kJ units when gas volume is increased to one mole at standard conditions (STP).

Solution:

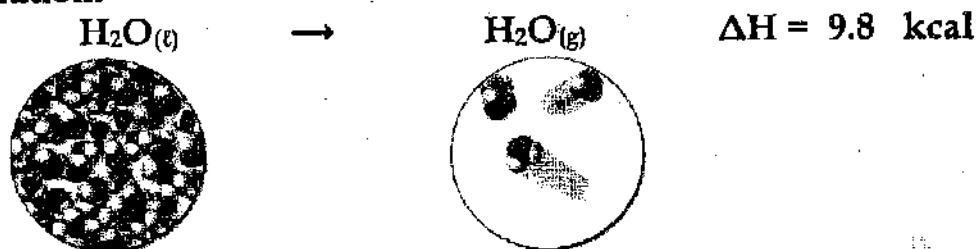
STP means that $P = 1 \text{ atm}$ and temperature is 273 K

1.0 mole of gas has a volume 22.4 L at (STP)

$$w = -22.4 \text{ L atm} \times \frac{101.39 \text{ J}}{\text{L atm}} = -231.93 \text{ J} = -2.3 \text{ kJ}$$

Example 13: Calculate the heat change at constant volume for vaporization of one mole of water at 100°C, knowing that the absorbed quantity of heat at constant pressure is 9.8 kcal.

Solution:



$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}} = 1 - 0.0 = 1 \text{ mol}$$

$$9.8 \times 4.184 \text{ kJ} = \Delta E + \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 373 \text{ K}}{1000 \frac{\text{J}}{\text{kJ}}}$$

$$41.0032 \text{ kJ} = \Delta E + 3.101 \text{ kJ}$$

$$\Delta E = 41.0032 \text{ kJ} - 3.101 \text{ kJ} = 37.902 \text{ kJ}$$

Example 13: The dissolving of zinc metal (Zn) in hydrochloric acid (HCl), the hydrogen gas is evolved according to the following equation:



At temperature 17°C, the accompanied heat is 36.2 kcal at constant pressure. Calculate the heat at constant volume for this system.

Solution:

$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

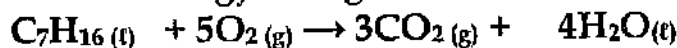
$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}} = 1 - 0.0 = 1 \text{ mol}$$

$$36.2 \times 4.184 \text{ kJ} = \Delta E + \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 290 \text{ K}}{1000 \frac{\text{J}}{\text{kJ}}}$$

$$151.46 \text{ kJ} = \Delta E + 2.411 \text{ kJ}$$

$$\Delta E = 151.46 \text{ kJ} - 2.411 \text{ kJ} = 149.04 \text{ kJ}$$

Example 13: The combustion of one mole of propane gas (C₃H₈) at constant pressure 2198.7 kJ at temperature 25°C and 1.0 atm, calculate the internal energy change at constant volume.



Solution:

$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$\Delta n_{(g)} = (n_{\text{products}} - n_{\text{reactants}})_{\text{gas}} = 3 - (1 + 5) = -3 \text{ mol}$$

$$2198.7 \text{ kJ} = \Delta E - \frac{3 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1000 \text{ J/kJ}}$$

$$2198.7 \text{ kJ} = \Delta E - 7.4327 \text{ kJ}$$

$$\Delta E = 2198.7 \text{ kJ} + 7.4327 \text{ kJ} = 2206.13 \text{ kJ}$$

The change in reaction heat is differing from one reaction to the other according to the following:

Different Types of Heat (Enthalpy) of Reaction

The heat or enthalpy changes accompanying chemical reactions are expressed in different ways, depending on the nature of the reaction. These are discussed below.

Heat of Formation

The heat of formation of a compound is defined as:

The change in enthalpy that takes place when one mole of the compound is formed from its elements.

It is denoted by ΔH_f . For example, the heat of formation of ferrous sulphide and acetylene may be expressed as:



Standard Heat Formation

The standard heat of formation of a compound is defined as:

The change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances being in their standard states (298 K and 1 atm pressure).

Notice that:

(i) The heat of formation of pure elements such as: $\text{Hg}_{(l)}$, $\text{Cl}_{2(g)}$, $\text{Na}_{(s)}$, $\text{Fe}_{(s)}$, $\text{N}_{2(g)}$ and $\text{Cu}_{(s)}$ are equal to zero at all temperatures.

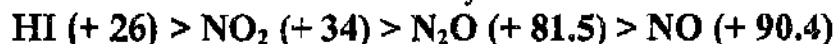
(ii) Almost of heat of formations are negative, which means that the heat of formation of compounds from its primary elements mostly is an exothermic reaction.

(iii) The compounds which are accompanied in their formation with exothermic heat are more stable because the heat content of product compound is less than the total heat content of the reacting elements in their compositions such as CH_4 , CH_3OH , ... etc.

(iv) As the free heat increased the stability of the produced compound is increased, consequently it is difficult to be dissociated.



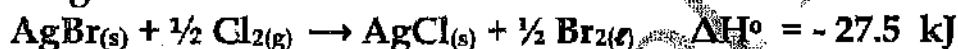
As the absorbent heat is increased the stability of formed compound is decreased, i.e.; it is easy to be dissociated.



The first law of thermodynamic allows the calculations of enthalpy change or reaction enthalpy at standard conditions (ΔH°) from the standard molar of formation enthalpies from the following equation:

$$\Delta H^\circ = \sum n_P \Delta H_f^\circ + \sum n_R \Delta H_f^\circ \quad (3)$$

Example 14: Calculate the standard enthalpy of formation at temperature 298 K for silver bromide ($\text{AgBr}_{(s)}$) depending on the following reaction:



Knowing that $\Delta H_f^\circ = -127.0 \text{ kJ mol}^{-1}$

Solution:

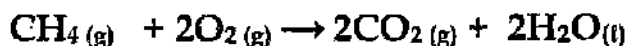
$$\begin{aligned} \Delta H^\circ &= [\Delta H_f^\circ(\text{AgCl}_{(s)}) + \frac{1}{2} \Delta H_f^\circ(\text{Br}_{2(l)})] - [\Delta H_f^\circ(\text{AgBr}_{(s)}) + \frac{1}{2} \Delta H_f^\circ(\text{Cl}_{2(g)})] \\ \Delta H^\circ &= -27.5 \text{ kJ} \\ -27.5 \text{ kJ} &= [-127 + 0.0] - [\Delta H_f^\circ(\text{AgBr}_{(s)}) + 0.0] \end{aligned}$$

Do some arrangements, we get the following:

$$\Delta H_f^\circ(\text{AgBr}_{(s)}) = -99.5 \text{ kJ}$$

Notice that the standard enthalpies of formation of bromine and chlorine liquids are consider equal to zero because they are elements and in their standard conditions.

Example 15: Calculate the heat of reaction ΔH° for the following reaction:



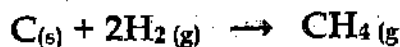
Knowing that the enthalpies of formation are:

$$\begin{aligned} \Delta H_f^\circ \text{CH}_{4(g)} &= -74.9 \text{ kJ} & \Delta H_f^\circ \text{O}_{2(g)} &= 0.0 \text{ kJ} \\ \Delta H_f^\circ \text{CO}_{2(g)} &= -393.5 \text{ kJ} & \Delta H_f^\circ \text{H}_2\text{O}(l) &= -285.8 \text{ kJ} \end{aligned}$$

Solution:

$$\begin{aligned} \Delta H^\circ &= \underbrace{\sum n_P (\Delta H_f^\circ)_P}_{\text{Products}} - \underbrace{\sum n_R (\Delta H_f^\circ)_R}_{\text{Reactants}} \\ \Delta H^\circ &= [2\Delta H_f^\circ \text{CO}_{2(g)} + 2\Delta H_f^\circ \text{H}_2\text{O}(l)] - [\Delta H_f^\circ \text{CH}_4 + \Delta H_f^\circ \text{O}_2] \\ \Delta H^\circ &= [2(-393.5) + 2(-285.8)] - [(-74.9) + 2(0.0)] \\ \Delta H^\circ &= [-787 - 571.6] - [(-74.9)] = -1358.6 + 74.9 = -1283.7 \text{ kJ} \end{aligned}$$

Example 16: The formation of 1.0 g of methane gas ($\text{CH}_4(\text{g})$) from its primary elements at standard conditions 4.675 kJ are produced. Calculate the standard heat of formation of methane with kilo joule units.



Solution:

In case of calculation of the standard heat of formation, which means the formation heat of reaction of one mole of material? Therefore we must deal with moles not with grams.

∴ The formation of methane gas an energy 4.675 kJ is produced.

∴ The reaction is exothermic, consequently the enthalpy change has a negative sign (-ve) i.e.; $\Delta H = -4.675 \text{ kJ}$.

$$n_{\text{CH}_4} = \frac{w_{\text{CH}_4}}{M_{\text{CH}_4}} = \frac{1.0 \text{ g}}{16 \text{ g mol}^{-1}} = 0.0625 \text{ mol}$$

$$0.0625 \text{ mol CH}_4 \rightarrow -4.675 \text{ kJ}$$

$$1.0 \text{ mol CH}_4 \rightarrow \Delta H_f^\circ = ?$$

$$\Delta H_f^\circ = \frac{1.0 \text{ mol} \times -4.675 \text{ kJ}}{0.0625 \text{ mol}} = -74.8 \text{ kJ}$$

Example 17: Calculate the reaction energy of the following reaction:



Knowing that: $\Delta H_f^\circ \text{ NH}_3 = -46 \text{ kJ}$ & $\Delta H_f^\circ \text{ HF}(\text{g}) = -271 \text{ kJ}$ & $\Delta H_f^\circ \text{ NF}_3(\text{g}) = -114 \text{ kJ}$

Solution:

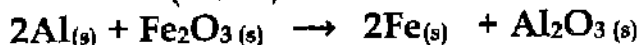
$$\Delta H^\circ = \underbrace{\sum n_P (\Delta H_f^\circ)_P}_{\text{Products}} - \underbrace{\sum n_R (\Delta H_f^\circ)_R}_{\text{Reactants}}$$

$$\Delta H^\circ = [\Delta H_f^\circ \text{ NF}_3 + 3\Delta H_f^\circ \text{ HF}] - [\Delta H_f^\circ \text{ NH}_3 + 3\Delta H_f^\circ \text{ F}_2]$$

$$\Delta H^\circ = [(-114) + 3(-271)] - [(-46) + 3(0.0)]$$

$$\Delta H^\circ = [-114 - 813] - [-46] = -927 + 46 = -881 \text{ kJ}$$

Example 18: Calculate the reaction energy of the following reaction knowing that the heat of formation of aluminium oxide (Al_2O_3) and ferric oxide (Fe_2O_3) are $-1676 - 822.7 \text{ kJ}$ respectively.



knowing that:

$$\Delta H_f^\circ \text{ Al}(\text{s}) = 0.0 \text{ kJ} \quad \& \quad \Delta H_f^\circ \text{ Fe}_2\text{O}_3(\text{s}) = -822.7 \text{ kJ}$$

$$\Delta H_f^\circ \text{ Fe}(\text{s}) = 0.0 \text{ kJ} \quad \& \quad \Delta H_f^\circ \text{ Al}_2\text{O}_3(\text{s}) = -1676 \text{ kJ}$$

Solution:

$$\Delta H^\circ = \underbrace{\sum n_P (\Delta H_f^\circ)_P}_{\text{Products}} - \underbrace{\sum n_R (\Delta H_f^\circ)_R}_{\text{Reactants}}$$

$$\Delta H^\circ = [2\Delta H_f^\circ \text{ Fe} + \Delta H_f^\circ \text{ Al}_2\text{O}_3] - [2\Delta H_f^\circ \text{ Al} + \Delta H_f^\circ \text{ Fe}_2\text{O}_3]$$

$$\Delta H^\circ = [2(0.0) + (-1676)] - [2(0.0) + (-822.7)]$$

$$\Delta H^\circ = [-1676] - [-822.7] = -1676 + 822.7 = -853.3 \text{ kJ}$$

Example 13: Calculate for the following equation:



Calculate the heat of formation of $\text{C}_6\text{H}_{22}\text{O}_{11}$, knowing that the heat of formation of water is -286 kJ/mol and for carbon dioxide is -393.5 kJ/mol .

Solution:

∵ The formation of $\text{C}_6\text{H}_{22}\text{O}_{11}$, an energy 5638.36 kJ is produced.

∵ The reaction is exothermic, consequently the enthalpy change has a negative sign (-ve) i.e.; $\Delta H = -5638.36 \text{ kJ}$.

$$\begin{aligned}\Delta H^\circ &= \underbrace{\sum n_P (\Delta H_f^\circ)_P}_{\text{Products}} - \underbrace{\sum n_R (\Delta H_f^\circ)_R}_{\text{Reactants}} \\ \Delta H^\circ &= [12\Delta H_f^\circ \text{CO}_2(\text{g}) + 11\Delta H_f^\circ \text{H}_2\text{O}] - [\Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11} + 12\Delta H_f^\circ \text{O}_2] \\ -5638.36 \text{ kJ} &= [12(-393.5) + 11(-285.8)] - [2\Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11}] \\ -5638.36 \text{ kJ} &= [-4722 - 3143.8] - [2\Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11}] \\ -5638.36 \text{ kJ} &= -7865.8 - [2\Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11}] \\ -5638.36 \text{ kJ} + 7865.8 &= -[2\Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11}] \\ 2227.44 &= -[2\Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11}] \\ 2\Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11} &= -2227.44 \text{ kJ} \\ \Delta H_f^\circ \text{C}_{11}\text{H}_{22}\text{O}_{11} &= \frac{-2227.44 \text{ kJ}}{2} = -1113.72 \text{ kJ}\end{aligned}$$

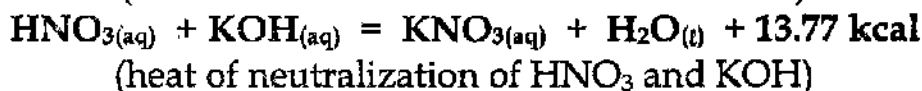
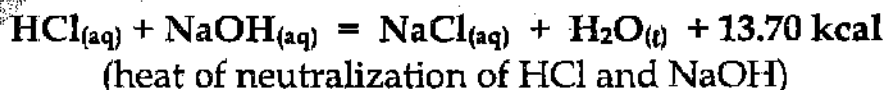
(2) Heat of Combustion

It is the amount of heat evolved on the combustion of one gram mole of the substance (or one gram atom of an element) in excess of O_2 .



(3) Heat of Neutralization

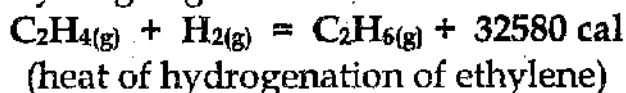
It is the quantity of heat evolved in the neutralization of one gram equivalent of an acid with one gram equivalent of the base from their dilute solutions.



It has been found that the heat of neutralization of all strong acids and bases is constant value and is equal to 13700 cal . In case of weak acids or weak bases, the heat of neutralization is less than 13700 cal . This will be explained in further details when dealing with the ionic theory.

(4) Heat of hydrogenation

It is the amount of heat evolved on the saturation of one gram mole of an unsaturated organic compound, e.g., ethylene or acetylene with hydrogen gas.



(5) Heat of Solution

It is the amount of heat evolved or absorbed when one gram mole of substance is dissolved in a quantity of sufficient solvent, to form a saturated solution only.

(6) Heat of Dilution

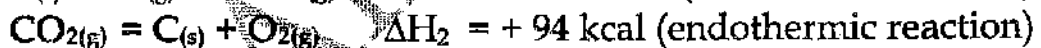
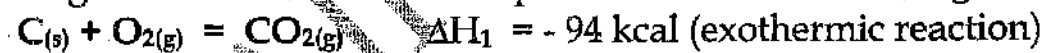
It is the amount of heat obtained when diluting the above mentioned solution until there is no heat change at infinite dilution.

Laws of Thermochemistry

These laws are based on the first law of thermodynamics which is based on the principle of conservation of energy that implies that "Energy cannot be created out of nothing".

First Law: Lavoisier and Laplace Law

The amount of heat necessary to decompose a certain compound into its constituent elements is equal to amount of heat evolved during the formation of this compound from its element, e.g.



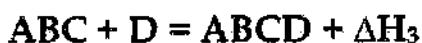
If ΔH_1 and ΔH_2 are not equal, it is clear that by adding the two equations, we can create energy out of nothing which is contradictory to the first law of thermodynamics.

Second Law: Hess's Law of constant heat summation

The heat of reaction (at constant pressure) is constant and does not depend on the intermediate steps of the reaction, i.e.; it is the same whether the reaction takes place in one step or in a number of steps, e.g., during the formation of the compound A B C D from the elements:



The reaction may be carried out in three steps as following:





According to Hess's Law:

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Practical Methods of Determination of Heat of Reaction:

(I) Heat of Combustion:

For the determination of heat of combustion the following system is used. It consists of a Bomb with thick steel walls plated with gold or platinum and provided with openings for the introduction of CO_2 . Inside the bomb a platinum crucible is present containing the substance whose heat of combustion is to be determined. The bomb is filled with O_2 under a pressure of several atmospheres. The substance is ignited by means of a platinum or iron wire which is heated by an electric current. The heat developed on combustion of the substance heats the water in which the bomb is immersed, and the change of temperature of the water in which the bomb is immersed and the change of temperature of the water is determined by means of a sensitive Beckmann thermometer as illustrated in Figure (2)

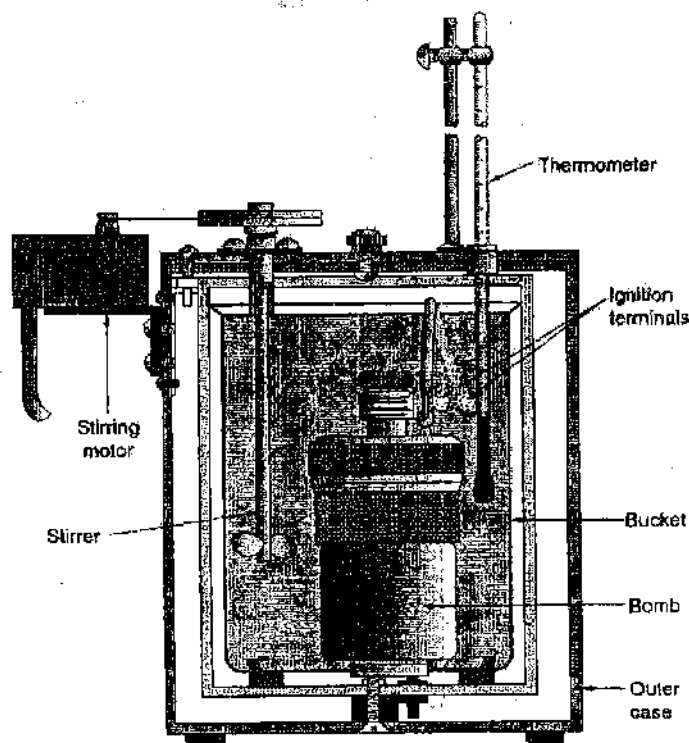


Figure (2) Pressure Volume Work

Method:

- (1) The sample is weighted perfectly, and is put in the isolated reaction container. Then the bomb is filled with oxygen gas.
- (2) The bomb container is immersed in quantity of or weighted water perfectly. Stirring the swater to get a homogenous temperature with all the calorimeter.
- (3) The temperature of the group is recorded (t_1).
- (4) The reaction is to be started using an electric arc.
- (5) The resultant heat is absorbed by the group and it will be recorded as (t_1).
- (6) Where both of water and bomb calorimeter absorb the produced heat, therefore the total heat capacity (C_t) is equal to the summation of water and bomb calorimeter capacities, i.e.;

$$C_{\text{total}} = C_{\text{Water}} + C_{\text{Calorimeter}}$$

The water heat capacity can be calculated from the weight of water used and the specific water heat but the heat capacity of the bomb calorimeter must be determined experimentally by measuring the increase of temperature of the bomb calorimeter as a result of its heating with known temperatures.

- (7) The produced heat of reaction can be calculated as a result of combustion from the total heat capacity (C_t) and the difference of temperature ($\Delta t = t_2 - t_1$) using the following equation:

$$q_{\text{Calorimeter}} = C_{\text{total}} \Delta t$$

Example 4: If 1.435 g of naphathene compound is burned in constant volume calorimeter contains 2000 g of water, the temperature is risen from 20.17°C to 25.84°C, if you know that the heat capacity of calometer (C_{Cal}) is 1.80 kJ/°C. The specific heat of water is 4.184 J/g °C. Calculate the following:

- (i) The released heat as a result of combustion.
- (ii) The released heat as result of combustion one mole of naphathalene.

Solution:

- (i) The acquired heat by water (q_w) can be calculated by the following equation:

$$\begin{aligned} q_{\text{water}} &= \rho \, m \, \Delta t = \rho \, m \, (t_2 - t_1) \\ q_w &= (4.184 \, \text{J/g } ^\circ\text{C}) \times (2000 \, \text{g}) \times (25.84 - 20.17) \, ^\circ\text{C} \\ q_w &= 4.74 \times 10^4 \, \text{J} = 47.4 \, \text{kJ} \end{aligned}$$

Then the acquired heat by the calorimeter can be calculated:

$$\begin{aligned} q_{\text{Calorimeter}} &= C_{\text{Cal}} \Delta t = (1.80 \, \text{kJ/}^\circ\text{C}) \times (25.84 - 20.17) \, ^\circ\text{C} \\ q_{\text{Calorimeter}} &= 1.02 \times 10^4 \, \text{J} = 10.2 \, \text{kJ} \end{aligned}$$

The acquired heat from the group (calorimeter and water) is:

$$q_{\text{total}} = q_w + q_{\text{Cal}} = 47.4 \text{ kJ} + 10.2 \text{ kJ} = 57.6 \text{ kJ}$$

$$q_{\text{total}} = q_w + q_{\text{Cal}}$$

The acquired heat by the group (calorimeter and water) is equal to the released heat as a result of burning, but different than it in sign, i.e.:

$$q_{\text{total}} = q_w + q_{\text{Cal}} = 47.4 \text{ kJ} + 10.2 \text{ kJ} = - 57.6 \text{ kJ}$$

(ii) From part (i) the released heat as a result of burning 1.435 g naphthalene and the molecular weight of naphthalene is 128.2 g. The released heat as a result of burning one mole of naphthalene is:

$$q = \frac{1.435 \text{ g (C}_{10}\text{H}_8) \Rightarrow -57.6 \text{ kJ}}{128.2 \text{ (C}_{10}\text{H}_8) \text{ g} \Rightarrow X (q)} = \frac{-57.6 \text{ kJ} \times 128.2 \text{ g (C}_{10}\text{H}_8)}{1.435 \text{ g mol}^{-1} \text{ (C}_{10}\text{H}_8)} = -5.15 \times 10^3 \text{ kJ/mol}$$

Example 5: If 100 mL of hydrochloric acid (0.5 M) is added to 100 mL sodium hydroxide (0.5 M) in calorimeter at constant pressure, its heat capacity is 335 J/°C. The primary temperature of the mixture is 22.5°C and the final is 24.9°C. Calculate the reaction enthalpy change assuming that the density and specific heat of the solution is equal to density and specific heat of water.

Solution:

If there is no loss of surrounding heat, the the reaction heat is:

$$q = - (q_{\text{solution}} + q_{\text{Calorimeter}})$$

where: q_{Solution} is acquired heat by the solution.

$$q_{\text{water}} = \rho m \Delta t = \rho m (t_2 - t_1)$$

$$q_{\text{Sol}} = (100 \text{ g} + 100 \text{ g}) \times 4.184 \text{ J/}^\circ\text{C} \times (24.9^\circ\text{C} - 22.5^\circ\text{C}) = 2.01 \times 10^3 \text{ J}$$

$$q_{\text{Calorimeter}} = C_{\text{Cal}} \Delta t = (335 \text{ kJ/}^\circ\text{C}) \times (4.9 - 2.5) ^\circ\text{C} = 804 \text{ J}$$

Subsequently:

$$q = - (2.01 \times 10^3 \text{ J} + 804 \text{ J}) = - 2.81 \times 10^3 \text{ J} = - 2.81 \text{ kJ}$$

$$\therefore \Delta H = - 2.81 \text{ kJ}$$

Example 2: If you know that 18.5 g of certain metal absorbed 1170 J of heat and its temperature is risen from 20°C to 92.5°C. Calculate the specific heat of this metal.

Solution:

The metal absorbed quantity of heat (q) is 1170 J, using the following equation, we get:

$$q = \rho m \Delta t \quad (3)$$

$$1170 \text{ J} = \rho \times 18.5 \text{ g} \times (92.5^\circ\text{C} - 25.0^\circ\text{C})$$

$$\text{Metal Specific heat } (\rho) = \frac{q}{m \times \Delta t}$$

$$\text{Metal Specific heat } (\rho) = \frac{1170 \text{ J}}{18.5 \text{ g} \times (92.5^\circ\text{C} - 25.0^\circ\text{C})} = 0.937 \text{ J/(g } ^\circ\text{C)}$$

Example 3: If 25 of a certain metal at temperature 90°C is added to 50 g water its temperature is 25.5°C . The temperature of water is risen to 29.9°C . If you know the specific heat of water is $4.184 \text{ J/g } ^\circ\text{C}$, calculate the specific heat of the metal.

Solution:

The quantity of acquired heat by water is equal to quantity of lost heat by the metal, therefore the quantity of acquired heat by water is:

$$\begin{aligned} q &= \rho m \Delta t \\ q &= \rho m (t_2 - t_1) \\ q &= \frac{4.184 \text{ J}}{\text{g } ^\circ\text{C}} \times 50.0 \text{ g} \times (29.8 - 25.0)^\circ\text{C} = 1004.16 \text{ J} \end{aligned}$$

The specific heat of the metal can be calculated, whereas the metal has lost the same quantity of heat which is acquired by water ($q = -1004.16 \text{ J}$) and the final temperature of the metal is the same of water, i.e.:

$$\begin{aligned} \Delta t &= (29.8 - 90)^\circ\text{C} = -60.2^\circ\text{C} \\ \rho(\text{Specific heat}) &= \frac{q}{m \Delta t} = \frac{-1004.16 \text{ J}}{25.0 \text{ g} \times (29.8 - 90.0)^\circ\text{C}} \\ \rho(\text{Specific heat}) &= \frac{-1004.16 \text{ J}}{25.0 \text{ g} \times -60.2^\circ\text{C}} = 66.7 \times 10^{-2} \text{ J/(g } ^\circ\text{C)} \end{aligned}$$

Student Exercise

1- The heat capacity of water is $1.0 \text{ cal g}^{-1} ^\circ\text{C}^{-1}$.

(i) Calculate the heat capacity by $\text{J g}^{-1} ^\circ\text{C}^{-1}$.

(ii) Calculate the necessary of heat quantity to rise the temperature of 100 g of water from 25°C to 100°C .

Solution:

(i) We know that: $1 \text{ cal} = 4.184 \text{ J}$

$$\text{The water heat capacity} = 1.0 \text{ cal g}^{-1} ^\circ\text{C}^{-1} \times \frac{4.184 \text{ J}}{\text{cal}} = 4.184 \text{ J g}^{-1} ^\circ\text{C}^{-1}$$

(ii) The necessary of heat quantity can be calculated as following:

$$\begin{aligned} q &= \rho m (t_2 - t_1) \\ q &= 100 \text{ g} \times 4.184 \text{ J g}^{-1} ^\circ\text{C}^{-1} \times (100 - 25)^\circ\text{C} = 31380 \text{ J} = 31.4 \text{ kJ} \end{aligned}$$

2- 50 g ice its temperature 0.0°C is added to 100 g water its temperature is 80°C . What is the final temperature of water at complete melting of ice? Assuming that there is no loss of

temperature to the external surrounding and knowing that the ice heat of fusion is 333 J g^{-1} and specific heat of water is $4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$.

Solution:

$$q_1 + q_2 = q_3 \quad (1)$$

Application of relation (2)

$$q_1 = 50.0 \text{ g} \times 333 \text{ J g}^{-1} \quad (4)$$

$$q_1 = \rho m \Delta t = \rho m (t_2 - t_1) \quad (2)$$

$$q_2 = 50.0 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1} (t - 0.0^{\circ}\text{C}) \quad (5)$$

$$q_3 = 100.0 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1} (80 - t^{\circ}\text{C}) \quad (6)$$

Compensating equations (4 - 6) into equation (1):

$$50.0 \text{ g} \times 333 \text{ J g}^{-1} + 50.0 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1} (t - 0.0^{\circ}\text{C}) = 100.0 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1} (80 - t^{\circ}\text{C})$$

$$16650 \text{ J} + (209.2 \text{ J }^{\circ}\text{C}^{-1}) \times (t - 0.0^{\circ}\text{C}) = (418.4 \text{ J }^{\circ}\text{C}^{-1}) (80^{\circ}\text{C} - t)$$

$$16650 \text{ J} + (209.2 \text{ J }^{\circ}\text{C}^{-1}) \times (t) = (33472 \text{ J}) - 418.4 \text{ J }^{\circ}\text{C}^{-1} (t)$$

$$(209.2 \text{ J }^{\circ}\text{C}^{-1}) \times (t) + 418.4 \text{ J }^{\circ}\text{C}^{-1} (t) = 33472 \text{ J} - 16650 \text{ J}$$

$$627.6 \text{ }^{\circ}\text{C}^{-1} \times (t) = 16822$$

$$\therefore t = 26.8^{\circ}\text{C}$$

3- A piece of aluminium metal its weight is 35 g and temperature 100°C is thrown in 320 g water its temperature is 23.75°C . What is the final temperature? If you know the specific heat of aluminium metal is $0.225 \text{ cal/g}^{\circ}\text{C}$.

We apply the thermal equilibrium principle, i.e; the quantity of lost heat by aluminum metal (q_{Al}) is the same quantity of heat which is acquired by water ($q_{\text{H}_2\text{O}}$). Assuming the final temperature is (t):

$$q = \rho m \Delta t = \rho m (t_2 - t_1)$$

$$q_{(\text{Al})} = 35.0 \text{ g} \times 0.226 \text{ cal g}^{-1} \text{ }^{\circ}\text{C}^{-1} \times (100^{\circ}\text{C} - t)$$

$$q_{(\text{Al})} = 7.91 \text{ cal g}^{-1} \text{ }^{\circ}\text{C}^{-1} \times (100^{\circ}\text{C} - t)$$

$$q_{(\text{Al})} = 791 \text{ cal} - 7.91 \text{ cal }^{\circ}\text{C}^{-1} (t) \quad (1)$$

$$q_{\text{H}_2\text{O}} = 320.0 \text{ g} \times 1 \text{ cal g}^{-1} \text{ }^{\circ}\text{C}^{-1} \times (t - 23.75^{\circ}\text{C})$$

$$q_{\text{H}_2\text{O}} = 320 \text{ cal }^{\circ}\text{C}^{-1} (t) - 7600 \text{ cal} \quad (2)$$

Egalitarian of (q_{Al}) and ($q_{\text{H}_2\text{O}}$), we get:

$$791 \text{ cal} - 7.91 \text{ cal }^{\circ}\text{C}^{-1} (t) = 320 \text{ cal }^{\circ}\text{C}^{-1} (t) - 7600 \text{ cal}$$

$$- 320 \text{ cal }^{\circ}\text{C}^{-1} (t) - 7.91 \text{ cal }^{\circ}\text{C}^{-1} (t) = - 791 \text{ cal} - 7600 \text{ cal}$$

$$- 320^{\circ}\text{C}^{-1} (t) - 7.91^{\circ}\text{C}^{-1} (t) = 7600 - 791$$

$$- 327.91 t^{\circ}\text{C}^{-1} = - 8391$$

$$\therefore t = 25.5893^{\circ}\text{C}$$

References:

- 1-Peter Atkins and Julio De Paula, Elements of Physical Chemistry - Ninth Edition - W.H.Freeman and Company New York - (2009).
- 2-Raymond Chang and Jason Overby, General Chemistry (The Essential Concepts) - Sixth Edition - Mc Graw Hill - (2008)
- 3- Thomas Engel and Philip Reid Engel Physical chemistry - Third Edition - Pearson - British Library Cataloguing-in-Publication Data - (2014)

