

Ministry of Higher Education  
and Scientific Research

Al-Muthanna University

College of Science

Department of Chemistry



وزارة التعليم العالي والبحث  
العلمي

جامعة المثنى

كلية العلوم

قسم الكيمياء

# Physical Chemistry

المحاضرة 2

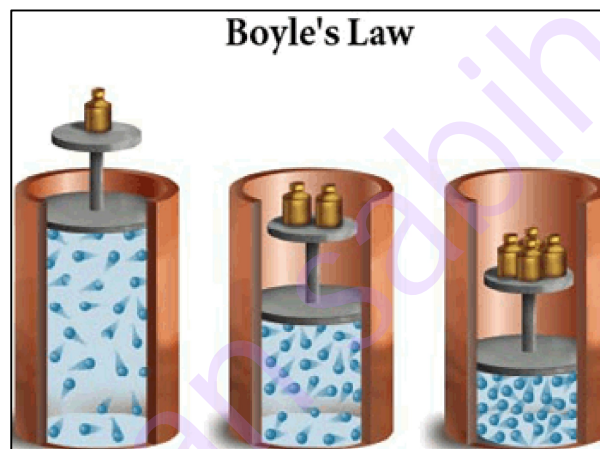
المرحلة الثانية

أ.د. حسن صبيح جبر

**Boyle's Law:**

In 1662, Robert Boyle discovered that there existed a relation between the pressure and the volume of a fixed amount of gas at a fixed temperature. In his experiment, he discovered that the product of Pressure & Volume of a fixed amount of gas at a fixed temperature was approximately a constant. So, Boyle's law states that

*"At constant temperature, the pressure of a fixed amount (i.e., number of moles  $n$ ) of gas varies inversely with its volume".*

**Mathematically**

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

$$P = k_1 \frac{1}{V} \Rightarrow PV = k_1 = \text{Constant}$$

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant.

If a fixed amount of gas at constant temperature  $T$  occupying volume  $V_1$  at pressure  $P_1$  undergoes expansion, so that volume becomes  $V_2$  and pressure becomes  $P_2$ , then according to Boyle's law :

$$P_1V_1 = P_2V_2 = \text{Constant} \Rightarrow \frac{P_1}{P_2} = \frac{V_1}{V_2}$$

Boyle's Law

**Question:**

A gas is present at a pressure of 2 atm. What should be the increase in pressure so that the volume of the gas can be decreased to  $\frac{1}{4}$  th of the initial value, If the temperature is maintained constant?

**Solution:**

PV = Constant for a given mass of gas at constant pressure

$$P_1V_1 = P_2V_2$$

$$P_1 = 2 \text{ atm}$$

$$V_1 = V$$

$$V_2 = V/4$$

$$2 \times V = P_2 \times V/4$$

$$P_2 = 8 \text{ atm}$$

Pressure should be increased from 2 to 8 atm.

Total increase =  $8 - 2 = 6$  atm

**Charles's Law :**

In 1787, Jacques Charles discovered that if the pressure is kept constant, the volume of a gas sample increases linearly with the temperature for a fixed amount of gas. This law led to the idea of temperature. The unit of temperature used is Kelvin. Charles's law states that

*"At constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature"*

**Mathematically**

$$V \propto T \Rightarrow V = kT$$

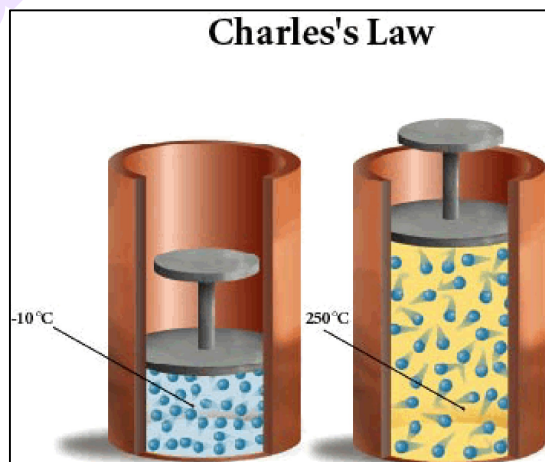
or

$$\frac{V}{T} = k = \text{constant}$$

Hence, if at constant pressure the volume of a gas  $V_1$  at temperature  $T_1$  change to  $V_2$  at  $T_2$  we have

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

This equation is known as **Charle's Law equation or formula.**



**Question:**

Volume of given amount of a gas at 57 °C and constant pressure is 425.8 cm<sup>3</sup>. If the temperature is decreased to 37 °C at constant pressure, then what would be the volume of gas?

**Solution:**

According to Charle's Law

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

Here

$$V_1 = 425.8 \text{ cm}^3$$

$$V_2 = ?$$

$$T_1 = 273 + 57 = 330 \text{ K}$$

$$T_2 = 273 + 37 = 310 \text{ K}$$

So,

$$V_2 = \frac{425.8 \times 310}{330} = 400 \text{ cm}^3$$

*Note/ In Charle's Law equation units of Temperature should be in kelvins*

**Gay-Lussac's Law or Amonation's Law :**

This law states that "at constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature".

**Mathematically**

$P \propto T$  (at constant volume)

$$\Rightarrow P = kT \Rightarrow \frac{P}{T} = k = \text{constant}$$

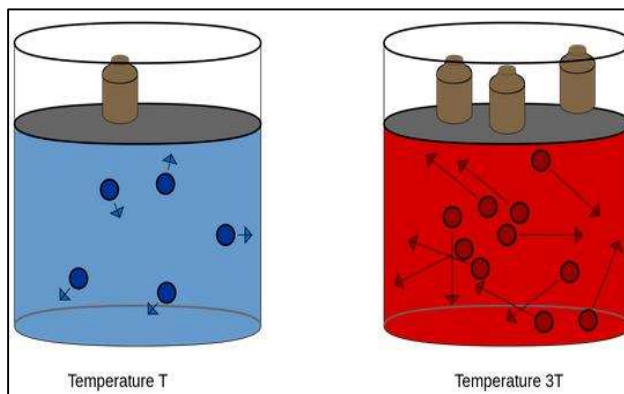
Where,

$P$  = Pressure of Gas

$T$  = Absolute Temperature

If the pressure and temperature of a gas changes from  $P_1$  &  $T_1$  to  $P_2$  &  $T_2$ , volume remaining constant, we have

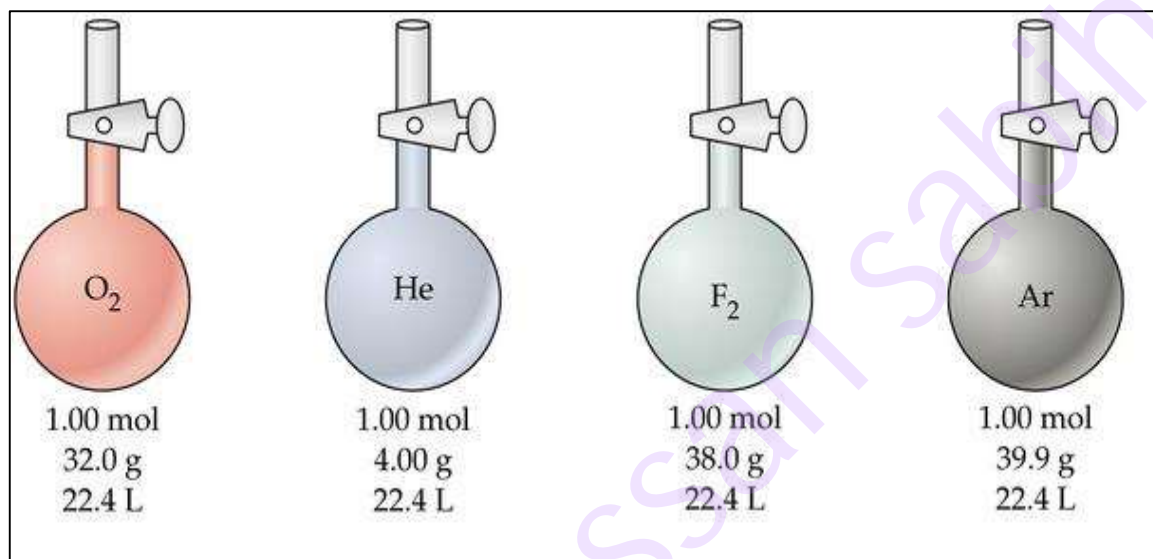
$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{constant}$$



#### 4. Avogadro's Law

In 1812, Amadeo Avogadro stated that

*“Samples of different gases which contain the same number of molecules (any complexity, size, shape) occupy the same volume at the same temperature and pressure”.*



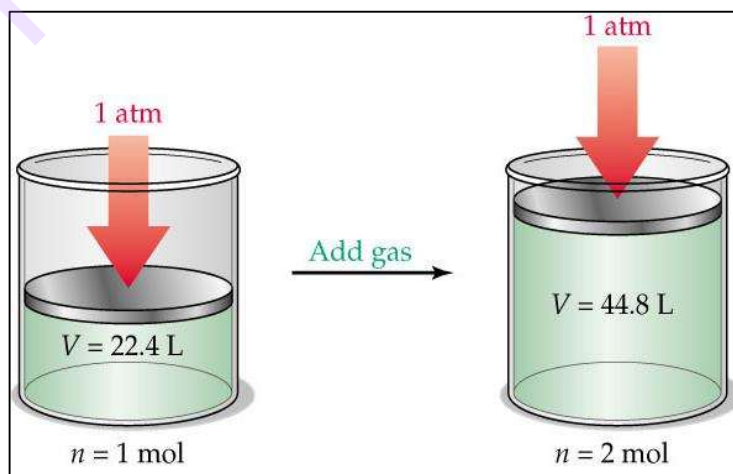
It follows from Avogadro's hypothesis that  $V \propto n$  (when T and P are constant).

#### Mathematically

$$V \propto n \Rightarrow V = kn$$

$$\Rightarrow \frac{V}{n} = k = \text{Constant}$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$



Since volume of a gas is directly proportional to the number of moles; **one mole of each gas at standard temperature and pressure (STP) will have same volume.** Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly  $10^5$  pascal) pressure.

Ex// If 4.00 L of gas at 1.22 atm is changed to 876 torr at constant temperature, what the final volume?

Ex// if 0.979 L of gas at 0°C is changed to 737 mL at constant pressure. What the final temperature?

H.W)

EX// A 20 L cylinder containing 6 atm of gas at 27 °C. What would the pressure of the gas be if the gas was heated to 77 °C

EX// A 6.0 L sample at 25 °C and 2.00 atm of pressure contains 0.5 moles of a gas. If an additional 0.25 moles of gas at the same pressure and temperature are added, what is the final total volume of the gas?

Q) Helium occupies 3.8 L at -45°C. What volume will it occupy at 45°C?

Q) A gas at STP is cooled to -185°C. What pressure in atmospheres will it have at this temperature (volume remains constant)?

Q) At 27°C, fluorine occupies a volume of 0.500 L. To what temperature in degrees Celsius should it be lowered to bring the volume to 200.0 mL?

### Combined Gas Equation

The Boyle's and Charles' law can be combined to give a relationship between the three variables P, V and T.

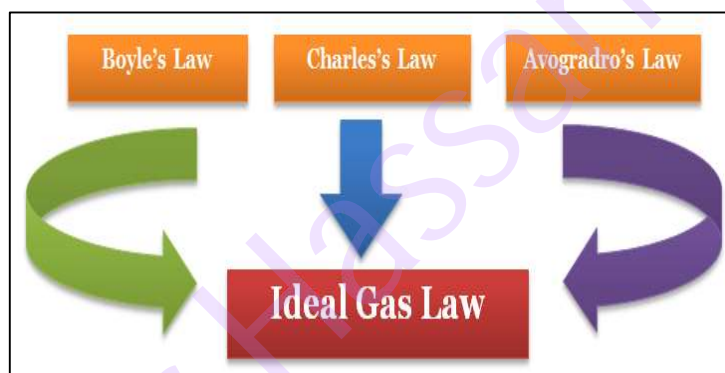
Let a certain amount of a gas in a vessel have a volume  $V_1$ , pressure  $P_1$  and temperature  $T_1$ .

On changing the temperature and pressure to  $T_2$  and  $P_2$  respectively, the gas occupies a volume  $V_2$ .

Then we can write

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

### Ideal Gas Equation



A gas that would obey Boyle's, Charles' law and Avogadro's law under the conditions of temperature and pressure is called an ideal gas.

Here, we combine four measurable variables P, V, T and n to give a single equation.

$V \propto n$ [P, T constant]	Avogadro's law
$V \propto T$ [n, P constant]	Charles's law
$V \propto 1/P$ [n, T constant]	Boyle's law

The combined gas law can be written as

$$V \propto nT / p$$

or  $pV \propto nT$

$$[ pV = nRT ] \text{ Ideal Gas Equation}$$



This is called **ideal gas equation**

where R is the constant of proportionality or universal gas constant

The value of R was found out to be

<b>Values of R</b>
0.082057 L atm mol <sup>-1</sup> K <sup>-1</sup>
62.364 L Torr mol <sup>-1</sup> K <sup>-1</sup>
8.3145 m <sup>3</sup> Pa mol <sup>-1</sup> K <sup>-1</sup>
8.3145 J mol <sup>-1</sup> K <sup>-1*</sup>
2 cal mol <sup>-1</sup> K <sup>-1</sup>

Ex// calculate the value of gas constant (R) if 1.00 mol of gas that occupies 22.4L at **STP**.

*Ans.* STP means 1.00 atm and 273 K (0°C). Thus,

$$R = \frac{PV}{nT} = \frac{(1.00 \text{ atm})(22.4 \text{ L})}{(1.00 \text{ mol})(273 \text{ K})} = 0.0821 \text{ L}\cdot\text{atm}/(\text{mol}\cdot\text{K})$$

#### **Relation between molar mass and density (From ideal gas equation)**

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

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

$$p = \frac{wRT}{MV} = \frac{\rho RT}{M}$$

- Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called **equation of state**.
- Ideal gas is a hypothetical concept. Real gases behave ideally only under certain conditions (i.e. high temperature and low pressure).

**EX//** A 3.0 L flask at 30.0°C contains 0.250 mole of Cl<sub>2</sub> gas.

- What is the pressure in the flask?
- What is the mass of the gas in the flask?
- What is the density of the chlorine gas in this flask?

**H.W//** A 5.0 L flask at 60.0°C contains 0.055 mole of oxygen gas.

- What is the pressure in the flask?
- What is the mass of the gas in the flask? if known the molar mass of oxygen is 32 gm/mole.
- What is the density of the oxygen gas in this flask?