



**Bonga University**  
**College of natural and computational science Department of**  
**chemistry**  
**Chemical Thermodynamics**  
**Lecture Note**

**INTRODUCTION TO GASES**

**1.1. INTRODUCTION**

In general matter is known to exist in one of the three states solid, liquid or a gas.

- A solid may be defined as a body possessing definite volume and shape at a given temperature and pressure.
- Solids are orderly arranged arrays of atoms, molecules or ions having definite geometry depending up on the arrangements of these atoms, molecules or ions.
- Solids are relatively rigid. The constituents are held together by strong attractive forces.
- A liquid on the other hand has a definite volume but no definite shape.
- Molecules consisting a liquid are held by molecular forces which are not as strong as solids.

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- Gases are important but usually unseen portion of the world around us.
- Gases have neither a shape nor a volume and the molecular forces of attraction are very much weaker. The most important gas sample to our existence as aerobic machines is the earth's atmosphere.
- Gases are conventionally classified in to two types, as ***Ideal gases*** and ***Real gases***.

### 2. Ideal gas and real gases

#### The equation of state

- The equation of state is an equation that describes the behaviour of mater in a given state.
- An equation of state is an equation relating states variables which describe the states of matter undergo a given set of physical conditions.
- An equation that relates the pressure, temperature and specific volume of substances.

Examples:

1. Equation of state for an ideal gas ( $PV = nRT$ )
2. Vander waals equation describes the behaviours of gases state.

### Ideal gas

An ideal gas is a hypothetical gas whose pressure- volume-temperature behaviour can be completely accounted for by the ideal equation.

An ideal gas is defined as one in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces. One can visualize it as a collection of perfectly hard spheres which collide but which otherwise do not interact with each other. In such a gas, all the [\*internal energy\*](#) is in the form of kinetic energy and any change in internal energy is accompanied by a change in [\*temperature\*](#).

#### Assumption of ideal gas

- The molecules in the gaseous state do not exert any force (either attractive or repulsive one another).

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- The volume of the molecules is negligibly small compared with that of the container (have no definite volume)
- Pressure is high and temperature is low.

### Gas Law Variables

An ideal gas is characterized by four state variables: **These commonly accepted gas law variables are: temperature, Pressure, Volume and number of moles.**

A state variable is a precisely measurable physical property which characterizes the state of a system, independently of how the system was brought to that state. It must be inherently single-valued to characterize a state. Some texts just use the term "thermodynamic variable" instead of the description "state variable"

### 1.3. The Gas Laws

#### Boyle's Law (The Pressure-Volume Relationship)

In the seventeenth century, the British chemist Robert Boyle studied the behaviour of gases systematically and quantitatively.

**Boyle's law**, which states that the pressure of a fixed amount of gas maintained at constant temperature is inversely proportional to the volume of the gas.

If the volume of a container is increased, the pressure decreases. If the volume of a container is decreased, the pressure increases, why?

Suppose the volume is increased. This means gas molecules have farther to go and they will impact the container walls less often per unit time. This means the gas pressure will be less because there are less molecule impacts per unit time. If the volume is decreased, the gas molecules have a shorter distance to go, thus striking the walls more often per unit time. This results in pressure being increased because there are more molecule impacts per unit time.

The mathematical expression showing an inverse relationship between pressure and volume is

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

Where the symbol means *proportional to*. To change r to an equals sign, we must write

$$P = k_1 \times \frac{1}{V} \dots\dots\dots 2$$

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if the applied pressure is decreased, the gas volume becomes larger.

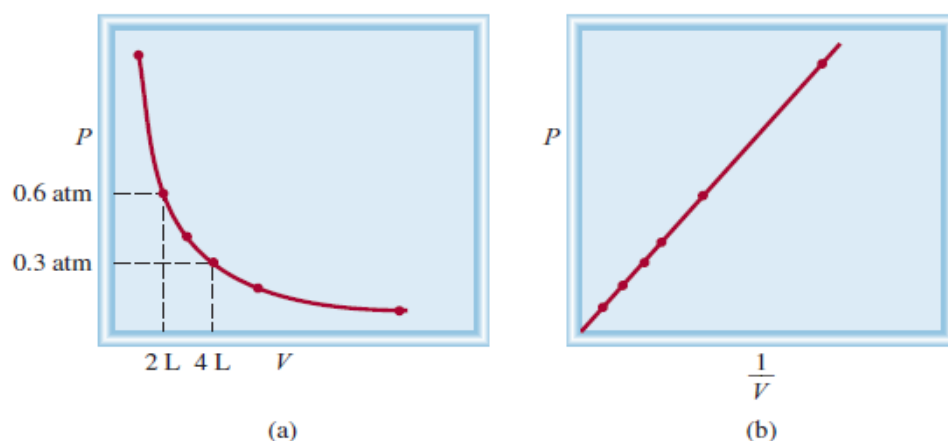
We can rearrange equation (2) and obtain

$$Pv = k$$

This form of Boyle's law says that the product of the pressure and volume of a Gas at constant temperature and amount of gas is a constant.

Figure 1 shows two conventional ways of expressing Boyle's findings graphically.

Figure 1(a) is a graph of the equation  $PV = k_1$ ; Figure 1(b) is a graph of the equivalent equation  $P = k_1 \times 1/V$ . Note that the latter is a linear equation of the form  $y = mx + b$ , where  $m = k_1$  and  $b = 0$ .



**Figure 1.** Graphs showing variation of the volume of a gas with the pressure exerted on the gas, at constant temperature. (a)  $P$  versus  $V$ . Note that the volume of the gas doubles as the pressure is halved. (b)  $P$  versus  $1/V$ .

For a given sample of gas under two different sets of conditions at constant temperature, we have

$$P_1V_1 = k_1 = P_2V_2$$

Or  $P_1V_1 = P_2V_2$  .....3

Where  $V_1$  and  $V_2$  are the volumes at pressures  $P_1$  and  $P_2$ , respectively.

### Charles's Law (the Temperature-Volume Relationship)

**Charles's law**, which states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas. If the volume of a

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container is increased, the temperature increases. If the volume of a container is decreased, the temperature decreases. Why?

Suppose the temperature is increased. This means gas molecules will move faster and they will impact the container walls more often. This means the gas pressure inside the container will increase but only for an instant. Think of a short span of time. The greater pressure on the inside of the container walls will push them outward, thus increasing the volume. When this happens, the gas molecules will now have farther to go, thereby lowering the number of impacts and dropping the pressure back to its constant value.

The dependence of the volume of a gas on temperature is given by

$$V \propto T$$
$$V = k_2 T$$

$$\text{Or } \frac{V}{T} = k_2 \dots\dots\dots 4$$

Where  $k_2$  is proportionality constant.

Just as we did for pressure-volume relationships at constant temperature, we can compare two sets of volume-temperature conditions for a given sample of gas at constant pressure. From Equation (4) we can write

$$\frac{V_1}{T_1} = k_2 = \frac{V_2}{T_2}$$

$$\text{Or } \frac{V_1}{T_1} = \frac{V_2}{T_2} \dots\dots\dots 5$$

Where  $V_1$  and  $V_2$  are the volumes of the gas at temperatures  $T_1$  and  $T_2$  (both in kelvins), respectively.

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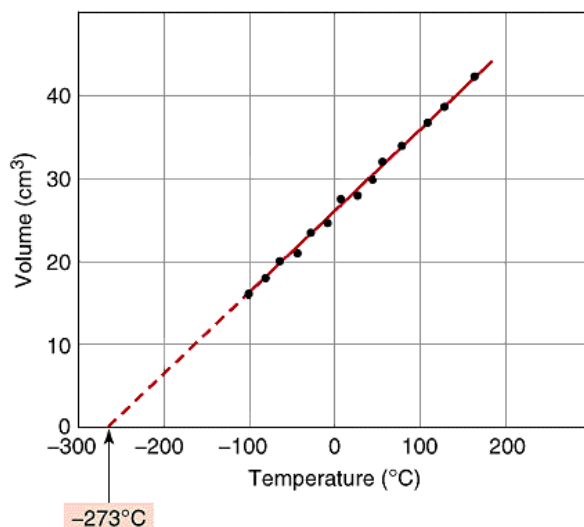


Figure 1.3. The Volume vs Temperature relationship for a gas at constant pressure (Charles' Law)

To the left of the intercept in the graph a gas would have a negative volume, which is impossible. Every time we make this experiment happen, every gas we use gives the same value of temperature for this intercept,  $-273^{\circ}\text{C}$ . The behavior of gases tells us something very unique which is called the **absolute zero** temperature ( $-273^{\circ}\text{C}$  or 0 K).

Another form of Charles's law shows that at constant amount of gas and volume, the pressure of a gas is proportional to temperature.

$$\begin{aligned} P &\propto T \\ P &= k_3 T \\ \text{Or } \frac{P}{T} &= k_3 \end{aligned} \quad \text{.....6}$$

From equation (6)

$$\frac{P_1}{T_1} = K_3 = \frac{P_2}{T_2} \text{ or } \frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{.....7}$$

Where  $P_1$  and  $P_2$  are the pressures of the gas at temperatures  $T_1$  and  $T_2$ , respectively.

### Avogadro's Law (the Volume-Amount Relationship)

**Avogadro's law**, which states that at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.

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If the amount of gas in a container is increased, the volume increases. If the amount of gas in a container is decreased, the volume decreases. Why?

Suppose the amount is increased. This means there are more gas molecules and this will increase the number of impacts on the container walls. This means the gas pressure inside the container will increase (for an instant), becoming greater than the pressure on the outside of the walls. This causes the walls to move outward. Since there is more wall space the impacts will lessen and the pressure will return to its original value.

$$V \propto n$$

$$V = k_4 n \dots \dots \dots (8)$$

Where  $n$  represents the number of moles and  $k_4$  is the proportionality constant.

For two samples of gas at the same temperature and pressure, the relation between volumes and numbers of moles can be represented as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} (\text{constant } T, P)$$

### GAY-LUSSAC'S LAW

Discovered by Joseph Louis Gay-Lussac in the early 1800's. It gives the relationship between pressure and temperature when volume and amount are held constant. If the temperature of a container is increased, the pressure increases. If the temperature of a container is decreased, the pressure decreases. Why?

Suppose the temperature is increased. This means gas molecules will move faster and they will impact the container walls more often. This means the gas pressure inside the container will increase, since the container has rigid walls (volume stays constant).

Gay-Lussac's Law is a direct mathematical relationship. This means there are two connected values and when one goes up, the other also increases. The mathematical form of Gay-Lussac's Law is:

$$\frac{P}{T} = k$$

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This means that the pressure-temperature fraction will always be the same value if the volume and amount remain constant. Let  $P_1$  and  $T_1$  be a pressure-temperature pair of data at the start of an experiment. If the temperature is changed to a new value called  $T_2$ , then the pressure will change to  $P_2$ . Keep in mind that when volume is not discussed (as in this law), it is constant. That means a container with rigid walls.

It is important to know the PT data pairs obey a constant relationship, but it is not important for us what the exact value of the constant is. Besides which, the value of  $K$  would shift based on what pressure units (atm, mmHg, or kPa) you were using.

We know this:  $\frac{P_1}{T_1} = k$  And we know that  $\frac{P_2}{T_2} = k$  Since  $k = k$ , we can conclude that .

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{OR} \quad P_1 T_2 = P_2 T_1 \text{-----}(1.5)$$

This equation is called Gay-Lussac's Law

### COMBINED GAS LAW

To derive the Combined Gas Law, do the following:

Step 1: Write Boyle's Law:  $P_1 V_1 = P_2 V_2$

Step 2: Multiply by Charles Law:  $P_1 V_1^2 / T_1 = P_2 V_2^2 / T_2$

Step 3: Multiply by Gay-Lussac's Law:  $P_1^2 V_1^2 / T_1^2 = P_2^2 V_2^2 / T_2^2$

Step 4: Take the square root to get the combined gas law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{-----}(1.9)$$

### **The ideal gas law equation: $PV = nRT = NKT$**

Let us summarize what we have learned about gases.

Any sample of gas can be described in terms of  $P$ ,  $T$ ,  $V$  and  $n$  present. Any three of these variables determine the fourth one.

We can summarize the behaviour of ideal gases as follows:



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Bolyle's law:

$$V \propto \frac{1}{P} \quad (\text{at constant } n \text{ and } T)$$

Charles's law  $V \propto T$  (at constant  $n$  and  $p$ )

Avogadro's law  $V \propto n$  (at constant  $T$  and  $P$ )

We can combine all three expressions to form a single master equation for the behaviour of gases:

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

$$V = R \frac{nT}{P} \quad \text{OR rearranging, } PV = nRT \dots \dots \dots 8$$

$n$  = number of [moles](#)

$R$  = universal gas constant = 8.3145 J/mol K = 0.08206 L atm / mol K = 1.987 cal / mol · K

$N$  = number of molecules

$k$  = Boltzmann constant =  $1.38066 \times 10^{-23}$  J/K =  $8.617385 \times 10^{-5}$  eV/K

$k = R/N_A$

$N_A$  = Avogadro's number =  $6.0221 \times 10^{23}$  /mol

**Note: the numerical value of  $R$ , the universal gas constant depends on the choices of the units for  $P$ ,  $V$  and  $T$ .**

### Dalton's Law of Partial Pressures

**Dalton's law of partial pressures**, which states that the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone.

Consider a case in which two gases, A and B, are in a container of volume  $V$ . The pressure exerted by gas A, according to the ideal gas equation, is

$$P_A = \frac{n_A RT}{V}$$

Where  $n_A$  is the number of moles of A present. Similarly, the pressure exerted by gas B is

$$P_B = \frac{n_B RT}{V}$$

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In a mixture of gases A and B, the total pressure  $P_T$  is the result of the collisions of both types of molecules, A and B, with the walls of the container. Thus, according to Dalton's law,

$$\begin{aligned}P_T &= P_A + P_B \\&= \frac{n_A RT}{V} + \frac{n_B RT}{V} \\&= \frac{RT}{V}(n_A + n_B) \\&= \frac{nRT}{V}\end{aligned}$$

Where  $n$ , the total number of moles of gases present, is given by  $n = n_A + n_B$ , and  $P_A$  and  $P_B$  are the partial pressures of gases A and B, respectively. For a mixture of gases, then,  $P_T$  depends only on the total number of moles of gas present, not on the nature of the gas molecules.

In general, the total pressure of a mixture of gases is given by

$$P_T = P_1 + P_2 + P_3 + \dots$$

Where  $P_1, P_2, P_3 \dots$  are the partial pressures of components 1, 2, 3  $\dots$

To see how each partial pressure is related to the total pressure, consider again the case of a mixture of two gases A and B. Dividing  $P_A$  by  $P_T$ , we obtain

$$\begin{aligned}\frac{P_A}{P_T} &= \frac{n_A RT / V}{(n_A + n_B) RT / V} \\&= \frac{n_A}{n_A + n_B} = X_A\end{aligned}$$

Where  $X_A$  is called the mole fraction of A. The **mole fraction** is a dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present.

The mole fraction is always smaller than 1. We can now express the partial pressure of A as

$$P_A = X_A P_T$$

Similarly,

$$P_B = X_B P_T$$

Note that the sum of the mole fractions for a mixture of gases must be unity. If only two components are present, then

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

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If a system contains more than two gases, then the partial pressure of the  $i^{\text{th}}$  component is related to the total pressure by,

$$\underline{P_i = X_i P_T}$$