University of Mosul
College of Science
Department of Physics
Second Stage

Heat and Thermodynamic

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Lecture 6: Equations of state

Preparation

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Chapter three

Equations of state

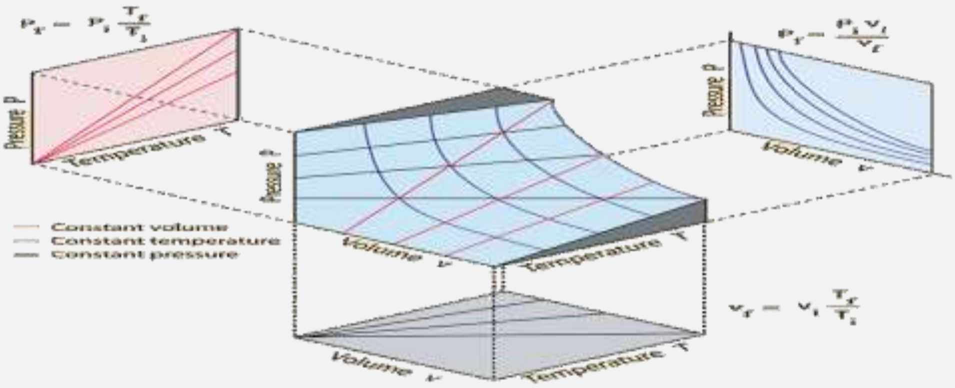
Here we focus on studying the state equations for pure substances in their vapor phase only, and this includes all what we call (unsaturated) gas that is highly roasted. The mixture of gases (air) can be considered a pure substance in its vapor phase because it possesses some characteristic properties of pure substances in its vapor phase which must be determined completely. In terms of specific size, pressure and temperature, it is considered one of the easiest materials that can be studied in thermodynamics. Such materials are called simple systems, which are usually gas

And state equation is a mathematical equation that relates the variables of a thermodynamic system. Experiment in thermodynamics shows that fixing some variables leads to the remaining variables having to take specified values, that is, randomness. An example of this is placing a certain gas in a closed vessel with a specific volume V present at a specified temperature T. Volume fixation means the constant mass of the gas m that can be used. In this case, by fixing T, the gas pressure P inside the vessel takes a specified value.

Mathematically, the relationship between the four previous variables can be expressed as follows: $f(P, V, T, m) = 0$

The previous equation is called the state equation for the system. It is possible, to write the equation of the previous state using the focused variables of the system by replacing the volume V with the specific, gram or molar, volume v and the equation becomes in the formula:

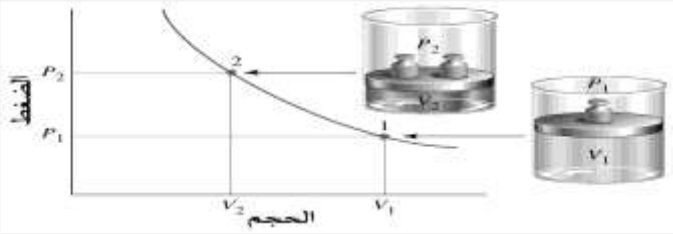
$$f(P, v, T) = 0$$



Ideal gas: a theoretical gas originally assumed to facilitate the study of thermodynamics, as well as for a simple approximation of the behavior of real gases, especially when they are in a state of permeation (low pressure). The mass M is used with the number of moles n, because one mole of any element in nature contains the same number of molecules, while mass M does not contain the same number of molecules.

There is another definition of an ideal gas: It is a gas that follows the following laws :

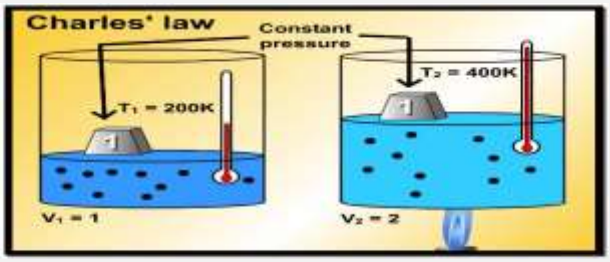
Boyle's law : is one of the laws of gases on the basis of which the ideal gas law was derived. It states that the volume of a specified amount of gas is inversely proportional to the pressure applied to it when its temperature is constant $P\alpha 1/v$, PV = constant



PV = constant , $P_1V_1= P_2V_2=$ Constant

Charles's Law: The volume of a mass of gas is directly proportional to its absolute temperature when the pressure is constant.

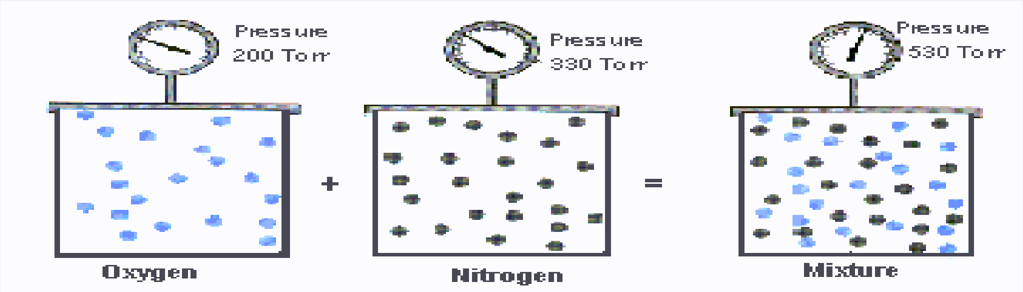
V/T =Constant or V α T



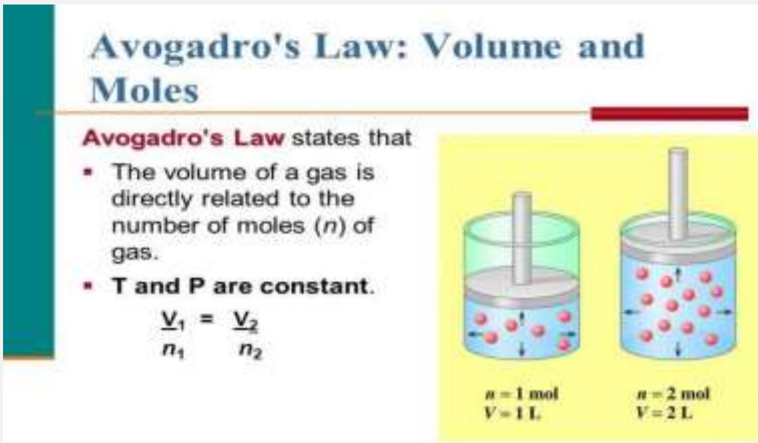
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = Constant$$

Dalton's law : states that the total pressure of a mixture of gases not interacting with each other is equal to the sum of the partial pressures of the gases that make up the mixture.

$P_{Total} = P_1+P_2+P_3+$……………….



Avogadro's law: equal volumes of different gases under the same conditions of temperature and pressure, containing the same number of molecules..



Avogadro's Law: Volume and Moles

Avogadro's Law states that

- The volume of a gas is directly related to the number of moles (n) of gas.
- **T and P are constant.**

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

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

Joule's Law: The internal energy of an ideal gas depends only on the temperature of the gas,

u = F (T)

The state equation for an ideal gas:

There are two ways to form the state equation for an ideal gas

First: the theoretical method

Second: the experimental method

Theoretical method: This method is based on a mathematical analysis based on the assumptions of the general theory of ideal gases, which assumes the existence of a model of gas with the following conditions

1. Any sample of gas contains a very large number of particles (the number of Avogadro equals $6.03 * 10^{23}$ a molecule, and the argument occupied by this number of particles under the standard condition equals 22.4 liters.
2. Gas molecules behave like spherical, negligible, completely flexible and continuous random motion
3. Molecules are completely independent of each other and there is no form of interaction between them, i.e. there is no mutual forces between the molecules.
4. The size of the particles themselves is completely neglected.
5. The average translational kinetic energy of particles is a direct measure of temperature $\frac{1}{2}mV^2 \; \alpha \; T$
6. In the absence of an external force, gas molecules spread uniformly throughout the space they occupy and move regularly in all directions
7. The collision time between collisions is small (it happens very quickly) compared to the time interval between collisions (there aren't many collisions)

Deriving the equation for an ideal gas: The pressure that the gas exerts on the walls of the vessel that contains it, and the result of the repeated collision of particles with the walls of the vessel and their reflection, which results at a change in the momentum of the particles. On the basis of Newton's second law of motion

(force = The rate of momentum change per unit projected onto the wall surface)

Pressure is $F = \frac{dP}{dt}$ equal to the force exerted per unit area

$$P = \frac{1}{3} m \left(\frac{N}{V}\right) \vartheta^2$$

m :mass of one molecular

N/V :No. of molecular per unit volume

ϑ^2 : mean square velocity

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

$$PV = \frac{2}{3} N \left(\frac{1}{2} m v^2\right) \ldots \ldots \ldots (1)$$

$\frac{1}{2} m V^2$ Mean kinetic energy

$\frac{1}{2} m V^2 = constant * T$ Condition 5

According to the kinetic theory of gases, the constant is equal to (3 /2 k)where k represents the Boltzmann constant

$$K = \frac{R}{N_0}$$

N_0 : number of molecules in mole (Avogadro's number 6.03 $*10^{23}$ mol $^{-1}$) R : universal gas constant

$$\frac{1}{2} m V^2 = constant * T$$

$$\frac{1}{2} m v^2 = \frac{3}{2} KT = \frac{3}{2} \frac{R}{N_0} T$$

We substitute in Equation No. 1 results

$$PV = \frac{2}{3} N.\left(\frac{3}{2}\frac{R}{N_o} T\right)$$

$$PV = \frac{N}{N_o} RT$$

N/N_0 = n : number of moles of gas

$$PV = n RT \ldots\ldots(2)$$

R is called the general constant for gas because it has the same value for all gases, it does not depend on the nature of the gas and it is equal to 8.317 $*10^3$ J/ Kmole.K

$$PV = RT$$

Whereas, V is the volume occupied by one mole of the gas at temperature T in Kelvin and pressure P.

State equation for real gas

From the above, we know that the behavior of an ideal gas can be represented by the simple relationship PV = RT . Since R is constant, the real gases does not follow this equation except under special conditions. It has been shown that real gases do not subscribe to the ideal gas equation, but rather deviate from the behavior of ideal gases The deflection is the greater the pressure exerted on the gas and the lower its temperature so that it does not exceed the critical temperature. That real gases, when they are subjected to special conditions of pressure and temperature, turn into a liquid and must therefore be represented

The state equation is the behavior of the fluid. Therefore, the equation PV = nRT will be modified to represent the behavior of real gases under all conditions of pressure and temperature.

Vanderwals Equation: One of the simplest and most popular equations for real gas, as this equation takes into consideration

1. The forces of attraction between molecules, which cannot be neglected, especially when the particles are close to each other under high pressures.

2. Real gas molecules have an actual volume that cannot be neglected under high pressures, as the volume occupied by the particles has become calculated in relation to the volume of the vessel that the gas contains.

so it became necessary to amend the state equation for the ideal gas and become as follows:

$$(\mathbf{P} + \Delta\mathbf{P})(\mathbf{V} - \Delta\mathbf{V}) = \mathbf{RT} \ldots\ldots(3)$$

ΔP :the amount of correction by volume resulting from taking into account the size of gas particles in consideration

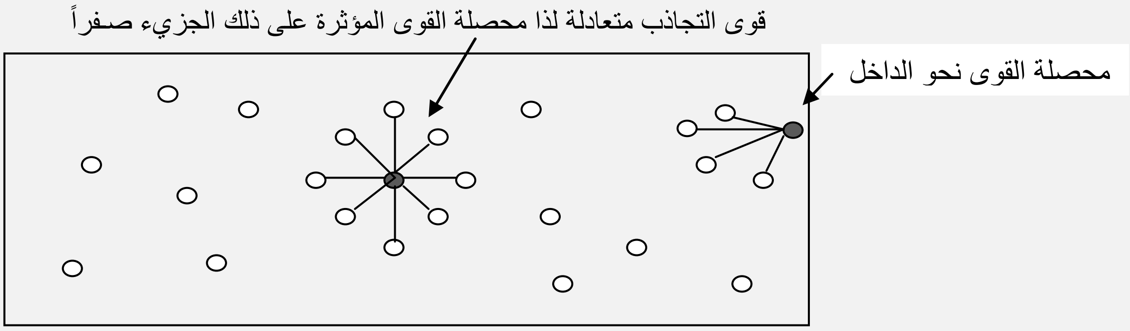
ΔV : the amount of correction by the pressure resulting from the attractive forces between gas molecules

Pressure Correction (D):

The molecule inside the gas is surrounded at any moment, in a large number of particles and equally from all sides.

And the attraction forces are equal in the movement of gas molecules in the container of all sides, and therefore the net result of the forces acting

on that molecule is zero. As a result, the molecule is free to move in all directions.



As for the molecule near the walls of the container, the resultant force acting on it is directed toward Inward, the molecule is drawn inward away from the walls, which reduces the pressure it places on Walls.

The actual pressure is less than the ideal pressure (which is the pressure that the gas would deliver if not There was no attraction between the molecules, that is, when the gas behaved ideally.

Therefore, a pressure correction of DP must be made proportional to the inward drag Which the internal particles shed on the particles close to the walls and the amount of correction depends There are two factors:

A- number of particles in the container, that is, the density of the gas ρ

B- number of strikes of particles on the unit inner surface of the container per unit time, and this depends the density of the gas also means that α ρ a : constant quantity that

$$\therefore\ \Delta P \alpha\, \rho^2 \qquad V = \frac{m}{\rho} \qquad v = \frac{V}{m} = \frac{1}{\rho} \qquad \therefore\ \Delta P = \frac{a}{v^2}$$

depends on the nature of the gas and

v : the molar specific volume

And since the ideal pressure = actual pressure + correction in pressure

$$(\mathbf{P} + \Delta\mathbf{P}) = \mathbf{p} + \frac{\mathbf{a}}{\mathbf{v}^2}$$

Volume correction (Δv): The volume of the container is all considered the volume at which the particles can move.

For an ideal gas, this assumption is that the size of the particles is negligible. While the size of the particles is calculated in the real gas. Therefore, not all of the volume of the container has room for the particles to move, Where b represents the amount of correction in volume which is four times the total volume of particles in the one mall.

$$\left(\mathbf{P}+\frac{\mathbf{a}}{\mathbf{v}^2}\right)(\mathbf{V}-\mathbf{b})=\mathbf{RT}\ldots\ldots(4)$$

Equation 4 is the state equation for real gases and is called the Van der Waals equation

Clausius equation: The effect of temperature on the holding forces between molecules is taken, and this equation takes the following mathematical form:

$$\mathbf{P}+\frac{\mathbf{a}}{\mathbf{T}(\mathbf{V}+\mathbf{c})^2}(\mathbf{V}-\mathbf{b})=\mathbf{RT}\ldots\ldots\ldots\ldots\ldots(5)$$

a,b,c constants depend on the nature of the gas