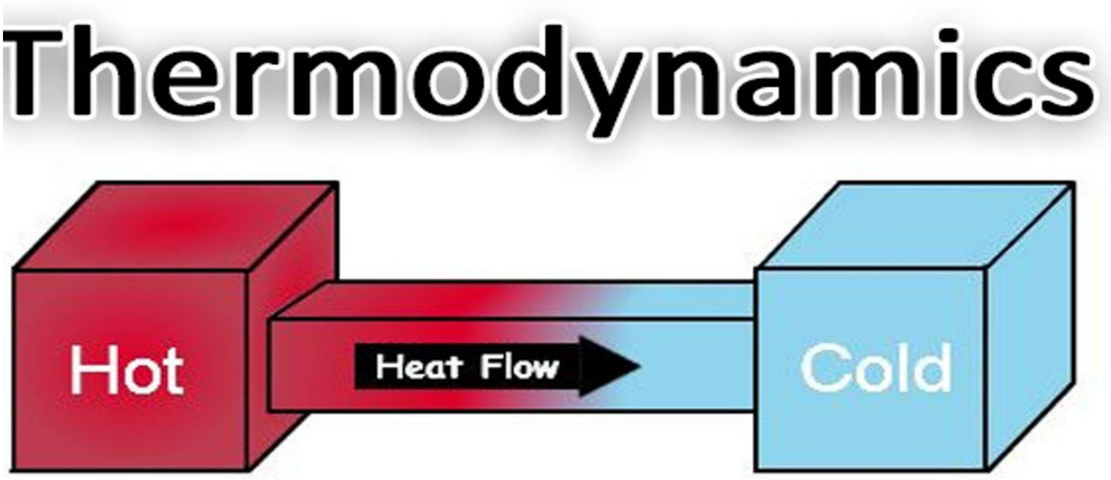
University of Baghdad

College of Science for women

Chemistry Department



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Introduction:

Rapid development of the study of external universe lead to the separation of chemistry as a special branch of natural science.

Chemical changes are always associated with a number of diversified physical changes like heat transfer, absorption or emission of electromagnetic radiations, electrical and surface phenomena.

Physical chemistry, branch **of chemistry concerned with interactions and transformations of materials**. Unlike other branches, it deals with the principles of physics underlying all chemical interactions (e.g., gas laws), seeking to measure, correlate, and explain the quantitative aspects of reactions.

Physical chemists are focused on understanding the physical properties of atoms and molecules, the way chemical reactions work, and what these properties reveal. Their discoveries are based on understanding chemical properties and describing their behavior using theories of physics and mathematical computations.

Thermodynamics is **the study of the relations between heat, work, temperature, and energy**. The laws of thermodynamics describe how the energy in a system changes and whether the system can perform useful work on its surroundings.

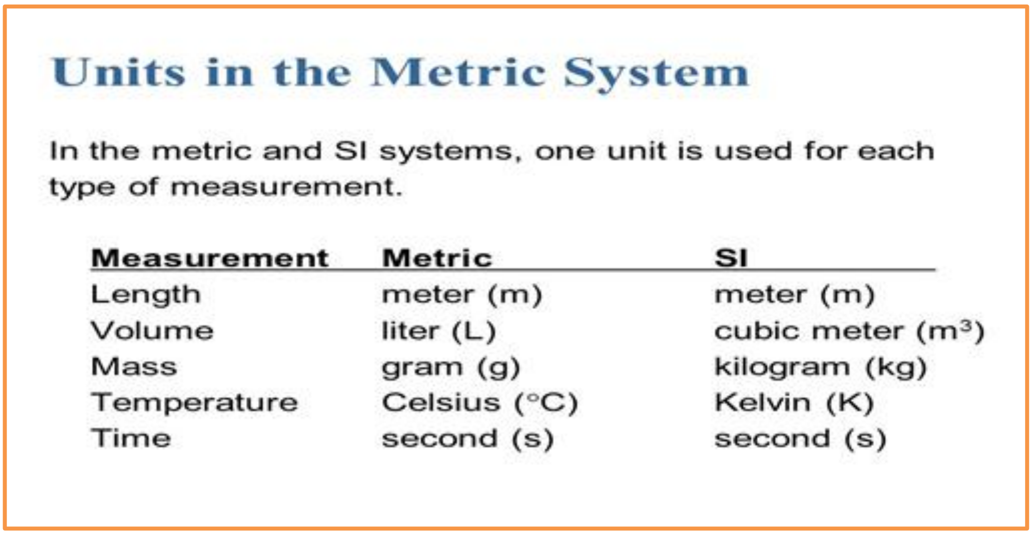
The most important laws of thermodynamics are:

- *The zeroth law of thermodynamics.* When two systems are each in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other. This property makes it meaningful to use thermometers as the “third system” and to define a temperature scale.

- *The first law of thermodynamics or the law of conservation of energy*. The change in a system's internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings.
- *The second law of thermodynamics*. Heat does not flow spontaneously from a colder region to a hotter region, or, equivalently, heat at a given temperature cannot be converted entirely into work. Consequently, the entropy of a closed system, or heat energy per unit temperature, increases over time toward some maximum value. Thus, all closed systems tend toward an equilibrium state in which entropy is at a maximum and no energy is available to do useful work.
- *The third law of thermodynamics*. The entropy of a perfect crystal of an element in its most stable form tends to zero as the temperature approaches absolute zero. This allows an absolute scale for entropy to be established that, from a statistical point of view, determines the degree of randomness or disorder in a system.

International system of Units (SI)

The **International System of Units** (**SI**, abbreviated from the French *Système international (d'unités)* is the modern form of the metric system. It is the only system of measurement with an official status in nearly every country in the world. It comprises a coherent system of units of measurement starting with seven base units, which are the second (the unit of time with the symbol s), meter (length, m), kilogram (mass, kg), ampere (electric current, A), kelvin (thermodynamic temperature, K), mole (amount of substance, mol), and candela (luminous intensity, cd**)**



Units in the Metric System

In the metric and SI systems, one unit is used for each type of measurement.

Measurement	Metric	SI
Length	meter (m)	meter (m)
Volume	liter (L)	cubic meter (m^3)
Mass	gram (g)	kilogram (kg)
Temperature	Celsius (°C)	Kelvin (K)
Time	second (s)	second (s)

Some principle derived from SI unit

Force	**Newton**	**N**	**Kg m s^{-2}**
Work, energy, quantity of heat	Joule	J	N.m= Kg m^2 s^{-2}
Pressure	Pascal	Pa	N m^{-2}

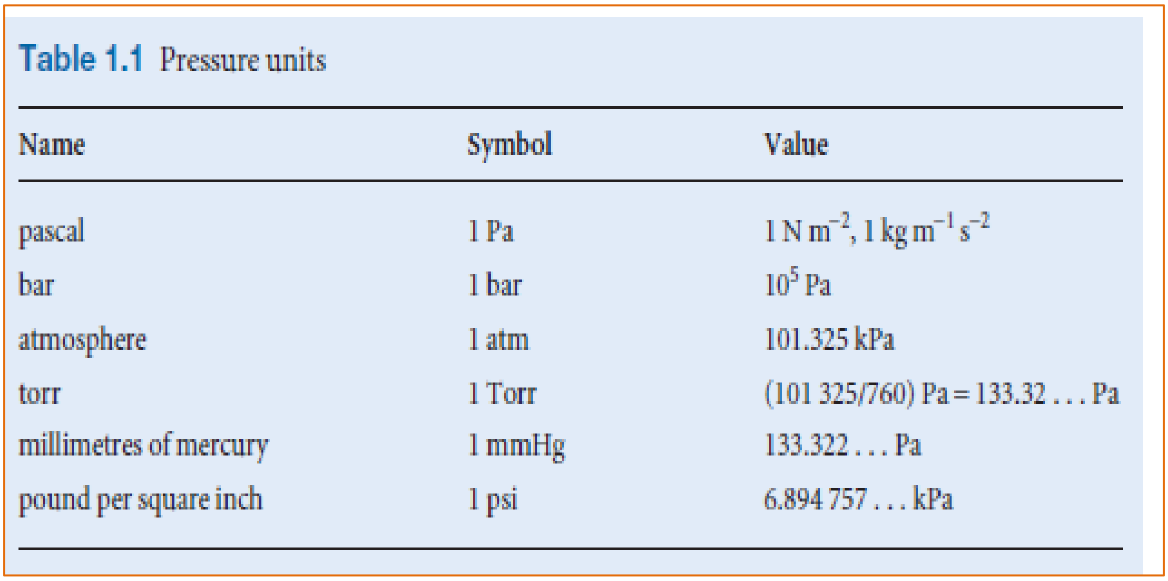
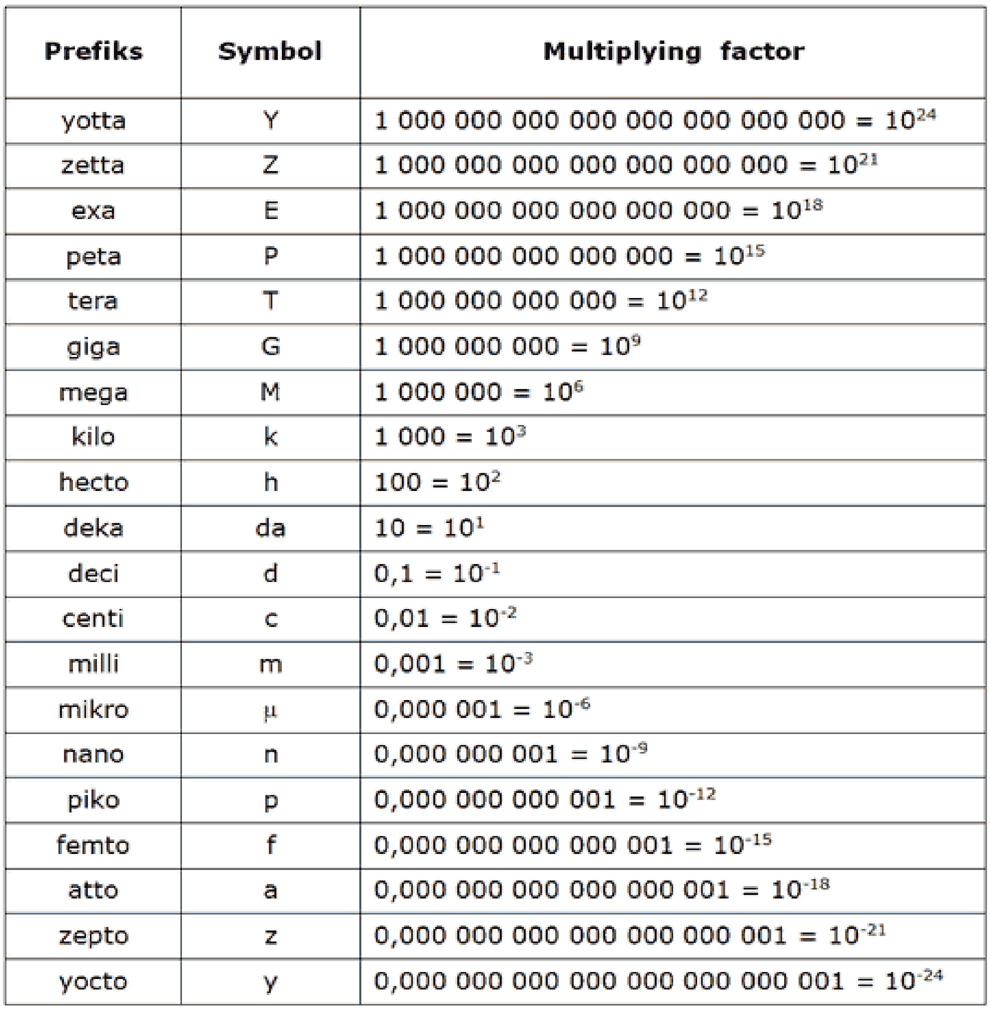


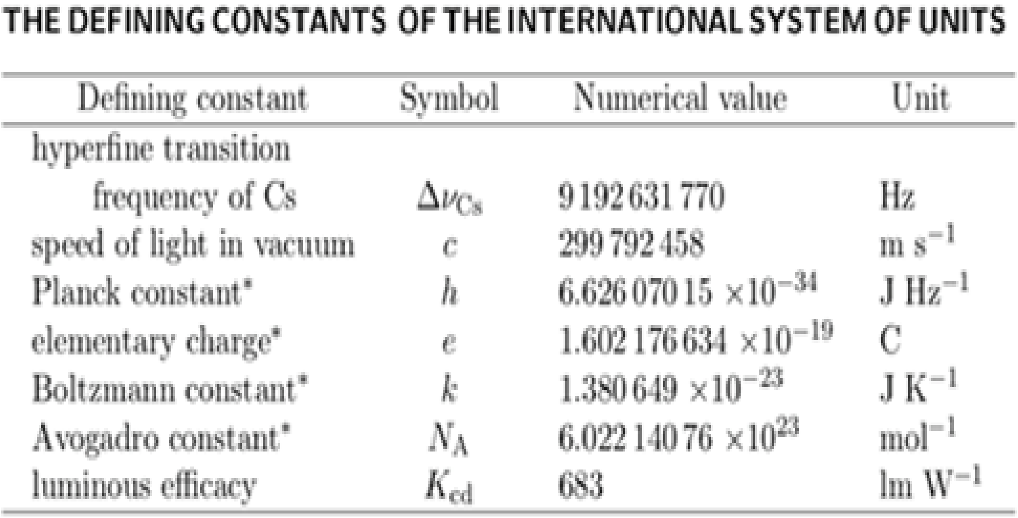
Table 1.1 Pressure units

Name	Symbol	Value
pascal	1 Pa	1 N m^{-2}, 1 kg m^{-1} s^{-2}
bar	1 bar	10^5 Pa
atmosphere	1 atm	101.325 kPa
torr	1 Torr	(101 325/760) Pa = 133.32 . . . Pa
millimetres of mercury	1 mmHg	133.322 . . . Pa
pound per square inch	1 psi	6.894 757 . . . kPa

Prefixes that modify of metric system of units



Prefiks	Symbol	Multiplying factor
yotta	Y	1 000 000 000 000 000 000 000 000 = 10^{24}
zetta	Z	1 000 000 000 000 000 000 000 = 10^{21}
exa	E	1 000 000 000 000 000 000 = 10^{18}
peta	P	1 000 000 000 000 000 = 10^{15}
tera	T	1 000 000 000 000 = 10^{12}
giga	G	1 000 000 000 = 10^{9}
mega	M	1 000 000 = 10^{6}
kilo	k	1 000 = 10^{3}
hecto	h	100 = 10^{2}
deka	da	10 = 10^{1}
deci	d	0,1 = 10^{-1}
centi	c	0,01 = 10^{-2}
milli	m	0,001 = 10^{-3}
mikro	µ	0,000 001 = 10^{-6}
nano	n	0,000 000 001 = 10^{-9}
piko	p	0,000 000 000 001 = 10^{-12}
femto	f	0,000 000 000 000 001 = 10^{-15}
atto	a	0,000 000 000 000 000 001 = 10^{-18}
zepto	z	0,000 000 000 000 000 000 001 = 10^{-21}
yocto	y	0,000 000 000 000 000 000 000 001 = 10^{-24}

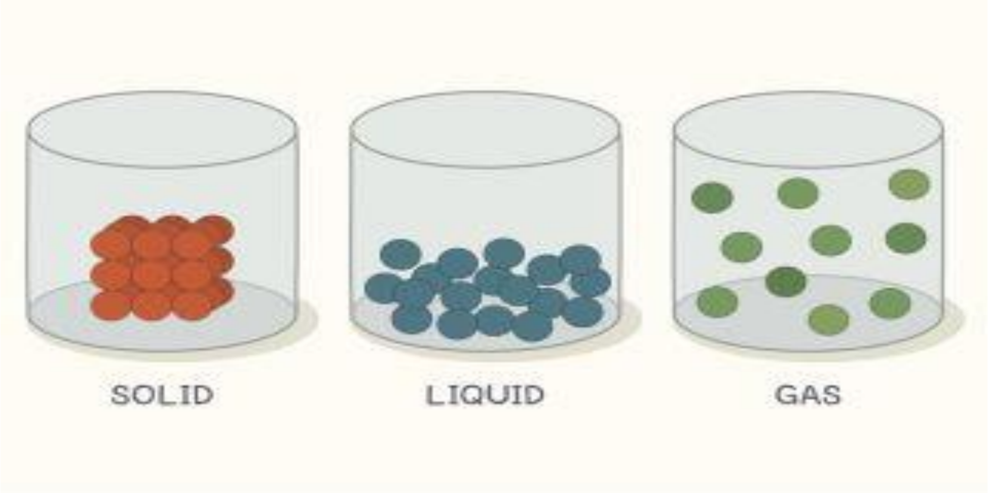


THE DEFINING CONSTANTS OF THE INTERNATIONAL SYSTEM OF UNITS

Defining constant	Symbol	Numerical value	Unit
hyperfine transition frequency of Cs	$\Delta\nu_{\mathrm{Cs}}$	9 192 631 770	Hz
speed of light in vacuum	c	299 792 458	m s^{-1}
Planck constant*	h	$6.626\,070\,15 \times 10^{-34}$	J Hz^{-1}
elementary charge*	e	$1.602\,176\,634 \times 10^{-19}$	C
Boltzmann constant*	k	$1.380\,649 \times 10^{-23}$	J K^{-1}
Avogadro constant*	N_{A}	$6.022\,140\,76 \times 10^{23}$	mol^{-1}
luminous efficacy	K_{cd}	683	lm W^{-1}

1. THE PROPERTIES OF GASES

Gas is a state of matter that has no fixed shape and no fixed volume. Gases have lower density than other states of matter, such as solids and liquids. There is a great deal of empty space between particles, which have a lot of kinetic energy. The particles move very fast and collide into one another, causing them to diffuse, or spread out, until they are evenly distributed throughout the volume of the container.



Gases are conveniently classified into two types, namely:

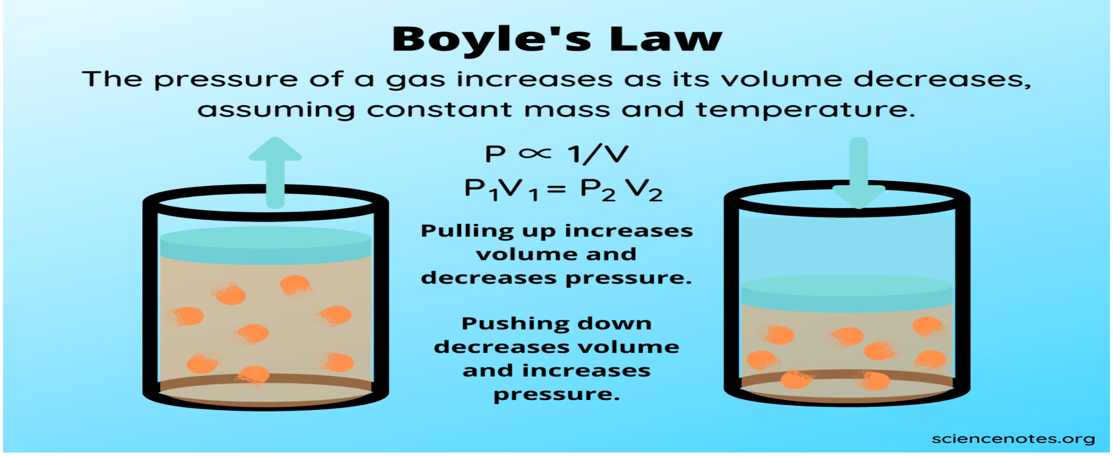
Ideal gas obeys all gas laws under all conditions of pressure and temperature.

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

Real gas or nonideal gas is defined as a gas that at all standard pressure and temperature conditions does not obey gas laws. It deviates from its ideal behaviour and obeys gas laws only at conditions of low pressure and high temperature. They obey Vander Waal's real gas equation.

1.1. Ideal Gas Behaviour

- **Boyle's law:** Boyle’s Law is a basic law in chemistry describing the behavior of a gas held at a constant temperature. The law, discovered by Robert A. Boyle in 1662, states that at a fixed temperature, the volume of gas is inversely proportional to the pressure exerted by the gas. In other words, when a gas is pumped into an enclosed space, it will shrink to fit into that space, but the pressure that gas puts on the container will increase.

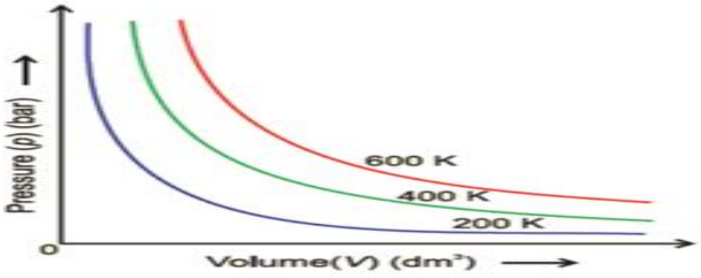


Mathematically:

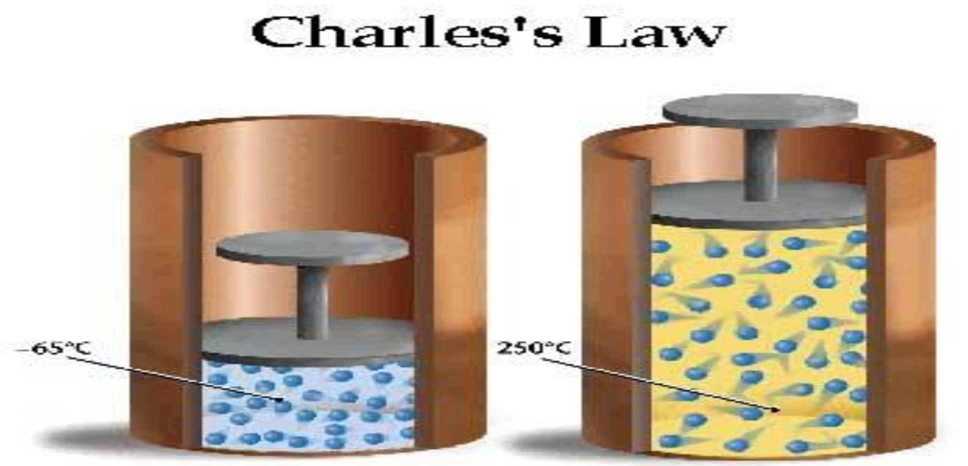
$$P \alpha \frac{1}{V} \qquad at\ constant\ temperature\ (T)$$

$$PV = constant$$

$$P_1V_1 = P_2V_2 \qquad or \qquad \frac{P_1}{P_2} = \frac{V_2}{V_1}$$



Charles's law: A statement that the volume occupied by a fixed amount of gas is directly proportional to its absolute temperature, if the pressure remains constant. This empirical relation was first suggested by the French physicist J.-A.-C. Charles about 1787**.**

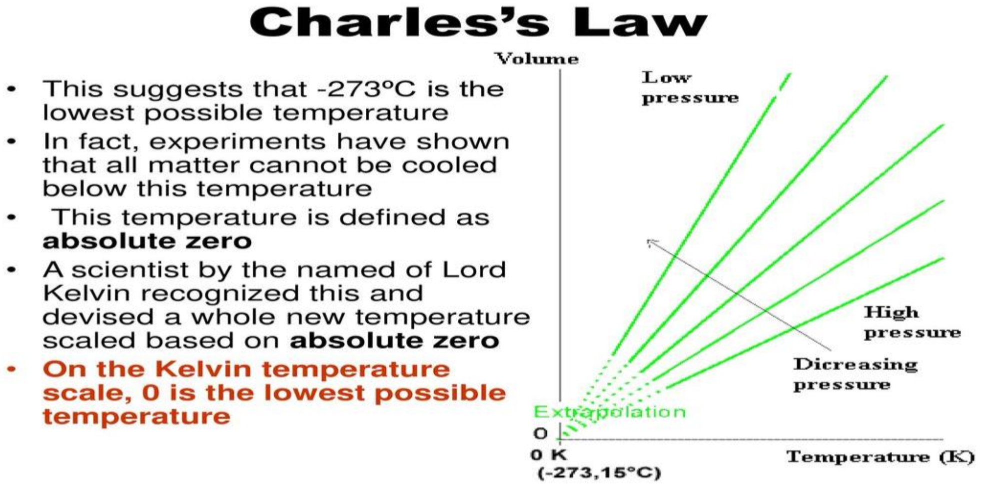


Mathematically:

$$V \alpha\, T \qquad at\ constant\ pressure\ (P)$$

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

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad or \qquad V_1T_2 = V_2T_1$$



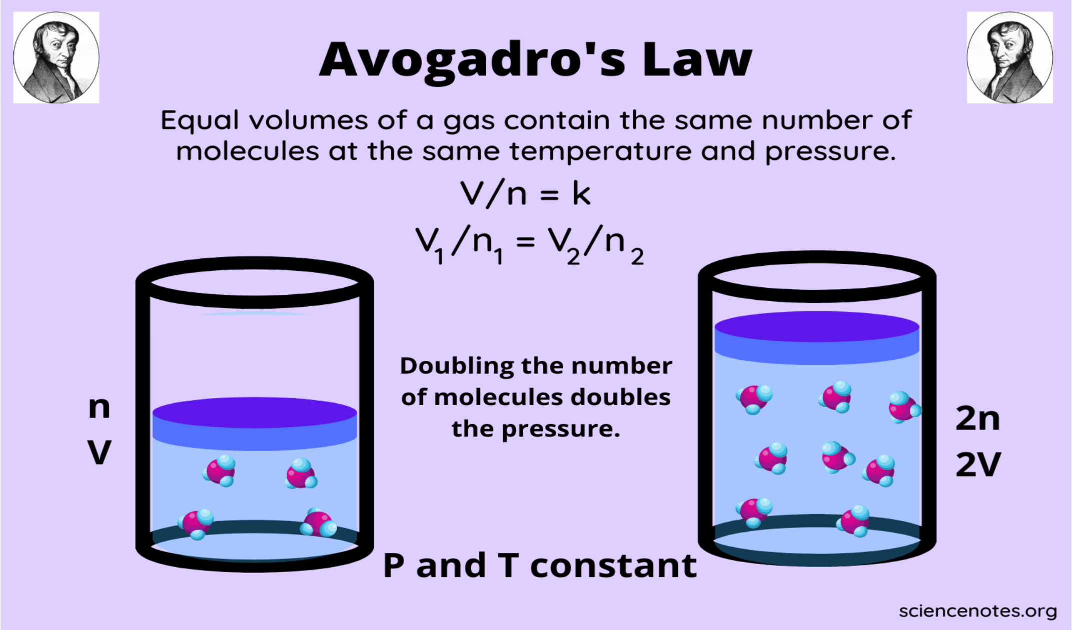
Charles's Law

- This suggests that -273°C is the lowest possible temperature
- In fact, experiments have shown that all matter cannot be cooled below this temperature
- This temperature is defined as **absolute zero**
- A scientist by the named of Lord Kelvin recognized this and devised a whole new temperature scaled based on **absolute zero**
- **On the Kelvin temperature scale, 0 is the lowest possible temperature**

- **Avogadro's law:**

Avogadro's law states that "equal volumes of all gases, at the same temperature and pressure, have the same number of molecules.

The law is named after Amedeo Avogadro who, in 1812, hypothesized that two given samples of an ideal gas, of the same volume and at the same temperature and pressure, contain the same number of molecules. As an example, equal volumes of gaseous hydrogen and nitrogen contain the same number of atoms when they are at the same temperature and pressure, and observe ideal gas behavior.



Mathematically:

$$V \,\alpha\, n \qquad at\ constant\ T\ and\ P$$

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

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

$N_A = 6.023 \times 10^{23}\ mol^{-1}$

Equation of State of an Ideal Gas

For ideal gas, the equation of states is PV equal to nRT. It is a result of combination of Boyle's and Charles's laws.

$$PV = constant$$

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

$$\frac{PV}{T} = constant$$

The value of constant was calculated at standard temperature, volume and pressure for one mole of any gas;

STP= Pressure= 1atm, temperature= 273.15 K, volume= 22.414 liters

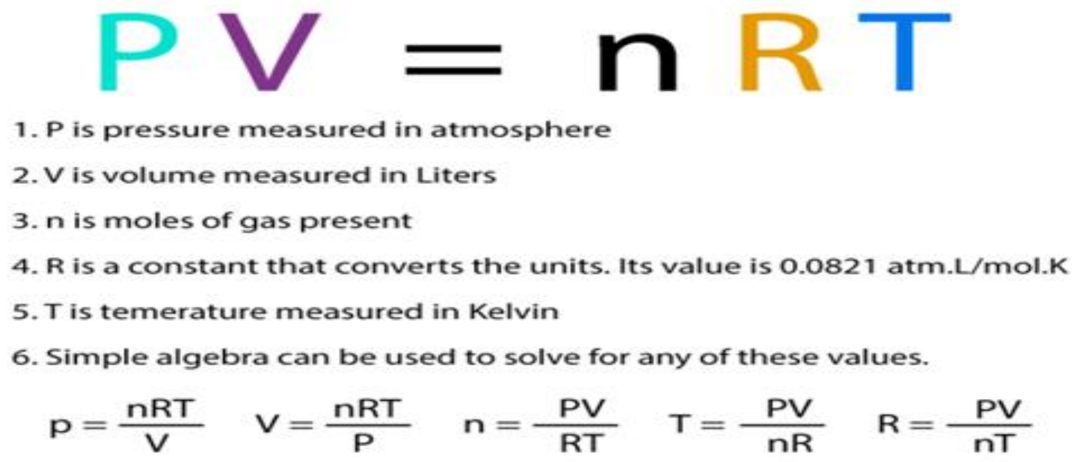
$$R = \frac{1atm \times 22.414L}{1\ mol\ \times 273.15K} = 0.08206\ \mathrm{L.atm.mol^{-1}.K^{-1}}$$

R= 8.314 x 10^{7}erg $\mathrm{mol^{-1}.K^{-1}}$

R= 8.314 J. $\mathrm{mol^{-1}.K^{-1}}$

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

Thermodynamic systems are specified by an equation of state that constrains the values that the state variables may assume. For a given amount of substance contained in a system, the temperature, volume, and pressure are not independent quantities; they are connected by a relationship of the general form.



$$PV = nRT$$

1. P is pressure measured in atmosphere
2. V is volume measured in Liters
3. n is moles of gas present
4. R is a constant that converts the units. Its value is 0.0821 atm.L/mol.K
5. T is temerature measured in Kelvin
6. Simple algebra can be used to solve for any of these values.

$$p = \frac{nRT}{V} \quad V = \frac{nRT}{P} \quad n = \frac{PV}{RT} \quad T = \frac{PV}{nR} \quad R = \frac{PV}{nT}$$

Applications of the Ideal Gas Law: Molar Mass, Density, and Volume

The volume occupied by one mole of a substance is its molar volume. The ideal gas law, $PV = nRT$, suggests that the volume of a given quantity of gas and the number of moles in a given volume of gas vary with changes in pressure and temperature. At standard temperature and pressure, or STP (273.15 K and 1 atm), one mole of an ideal gas (regardless of its identity) has a volume of about 22.4 L — this is referred to as the standard molar volume.

For example, one mole each of hydrogen, oxygen, argon, or carbon dioxide occupies 22.4 liters at STP. This implies that 0.5 moles of any gas at STP occupies a volume of 11.2 L, and similarly, 2 moles of any gas at STP occupies a volume of 44.8 L.

The ideal gas law is universal, relating the pressure, volume, number of moles, and temperature of a gas regardless of the chemical identity of the gas:

$$PV = nRT$$

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

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

$$M = \frac{wRT}{PV}$$

Density is the ratio of mass over volume. Rearranging the ideal gas equation to isolate *V* and substituting into the density equation yields:

$$\rho = \frac{w}{V}$$

$$M = \frac{\rho RT}{P}$$

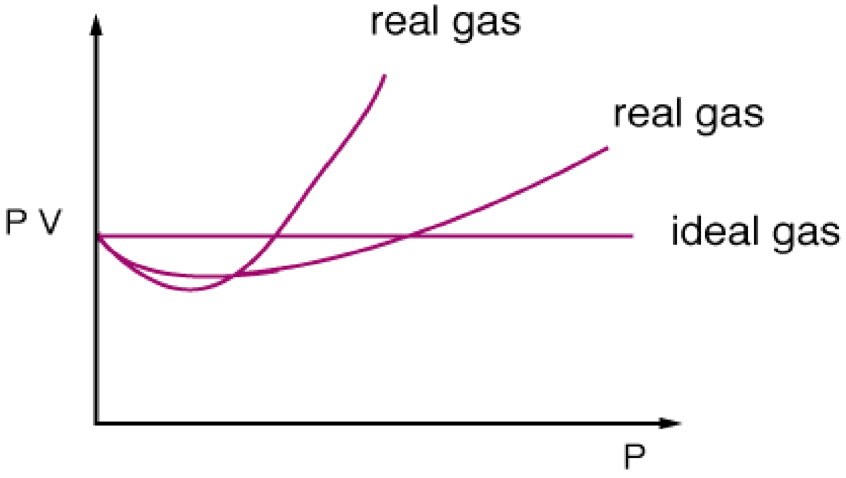
This equation tells us that gas density is directly proportional to the pressure and molar mass, and inversely proportional to the temperature. For example, CO_2 (molar mass = 44 g/mol) is heavier than N_2 (molar mass = 28 g/mol) or O_2 (molar mass = 32 g/mol), and is therefore denser than air. For this reason, CO_2 released from a CO_2 fire extinguisher blankets a fire, preventing O_2 from reaching the combustible material. The phenomenon of the lifting of hot air balloons depends on the relationship that gases of equal molar masses (such as air) have lower densities at higher temperatures, and therefore hot air balloons can float.

1.2. Real gases

Real gases do not obey the perfect gas law exactly. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid.

Real gases show deviations from the perfect gas law because molecules interact with one another. Repulsive forces between molecules assist expansion and attractive forces assist compression.

Intermolecular forces are also important when the temperature is so low that the molecules travel with such low mean speeds that they can be captured by one another.

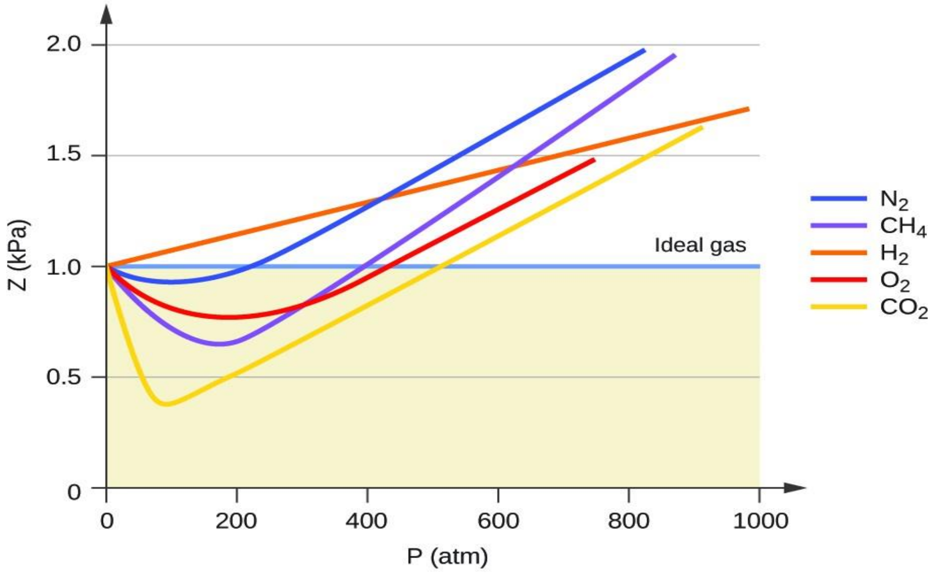


At low pressures, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly. At moderate pressures, when the average separation of the molecules is only a few molecular diameters, the attractive forces dominate the repulsive forces. In this case, the gas can be expected to be more compressible than a perfect gas because the forces help to draw the molecules together. At high pressures, when the average separation of the molecules is small, the repulsive forces dominate and the gas can be expected to be less compressible because now the forces help to drive the molecules apart.

Compressibility factor

In thermodynamics, the **compressibility factor** (**Z**), also known as the **compression factor** or the **gas deviation factor**, is a correction factor which describes the deviation of a real gas from ideal gas behaviour. It is simply defined as the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure. It is a useful thermodynamic property for modifying the ideal gas law to account for the real gas behaviour.

Alternatively, the compressibility factor for specific gases can be read from generalized compressibility charts that plot Z as a function of pressure at constant temperature.



One way in which the accuracy of $PV = nRT$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, V_m) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor**, **Z**, with:

$$Z = \frac{molar\ volume\ of\ gas\ at\ same\ T\ and\ P}{molar\ volume\ of\ ideal\ gas\ at\ same\ T\ and\ P} = \frac{PV_m}{nRT}$$

The value of Z generally increases with pressure and decreases with temperature. At high pressures molecules are colliding more often. This allows repulsive forces between molecules to have a noticeable effect, making the molar volume of the real gas V_m greater than the molar volume of the corresponding ideal gas (which causes Z to exceed one.

Because for a perfect gas $Z = 1$ under all conditions, deviation of Z from 1 is a measure of departure from perfect behaviour. At very low pressures, all the gases shown have $Z \approx 1$ and behave nearly perfectly. At high pressures, all the gases have $Z > 1$, signifying that they have a larger molar volume than a perfect gas. Repulsive forces are now dominant. At intermediate pressures, most gases have $Z < 1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.

The van der Waals equation of state

The van der Waals equation is an equation of state that corrects for two properties of real gases: the excluded volume of gas particles and attractive forces between gas molecules. The van der Waals equation is frequently presented as**:**

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

‘a’ and ‘b’ constants specific to each gas.

Van der Waals equation derivation is based on correcting the pressure and volume of the ideal gases given by the Kinetic Theory of Gases.

In practice, Van der Waals assumed that, gaseous particles –

1. Are hard spheres.
2. Have definite volume and hence cannot be compressed beyond a limit.

3. Two particles at close range interact and have an exclusive spherical volume around them.

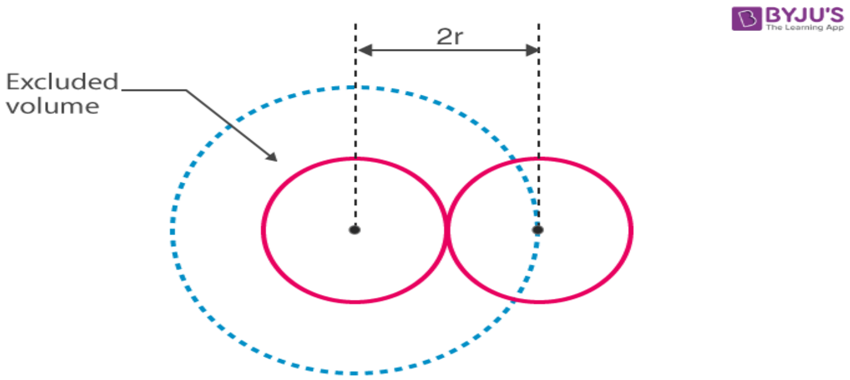
Volume Correction in Van der Waals Equation

As the particles have a definite volume, the volume available for their movement is not the entire container volume but less. Volume in the ideal gas is hence an overestimation and has to be reduced for real gases.

Volume of the real gas V_R = Volume of the container/ideal gas (V_I) – Correction factor(b) $V_R = V_I - b$.

But, the particles are not independent, they do interact.

Van der Waal considered two hard-sphere particles can come as close as to touch each other and they will not allow any other particle to enter in that volume as shown in the diagram.



Pressure Correction in Van der Waals Equation

Gaseous particles do interact. For inside particles, the interactions cancel each other. But, the particles on the surface and near the walls of the container do not have particles above the surface and on the walls. So, there will be net interactions or pulling of the bulk molecules towards the bulk that is away from the walls and surface. The molecules experiencing a net interaction away from the walls will hit the walls with less force and pressure. Hence, in real gases, the particles exhibit lower pressure than shown by ideal gases.

Consider a molecule in the interior of a gas, it is surrounded uniformly by other molecules so that there is no attraction on this molecules. When these molecules approached the wall of the vessel, this distribution of molecule is disturbed and attracted by molecules from one side only, so the molecules have a net inward pull and strike the wall of vessel with lower velocity and exert a lower pressure. The measured pressure P will thus be less than the ideal pressure. It is therefore necessary to add a correction term (P_a) to the observed pressure in order to obtain the ideal pressure.

Corrected (ideal pressure) $P_{ideal} = P + P_a$

This correction depends on:

1- The number of molecules in the bulk of the gas.

2- The number of molecules striking the wall per unit area.

Both these factors are proportional to the number of molecules per unit volume (n/V) Hence, the correction term P_a is:

$$P_a \propto \left(\frac{n}{V}\right)^2$$

$$P_a = \frac{aV^2}{n^2}$$

$$P_{ideal} = P + \frac{an^2}{V^2}$$

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

The constant (a and b) are known as the Vander Waals constant. They have positive values and are specific to each gas. The term involving the constant a corrects for intermolecular attraction. Attractive forces between molecules decrease the pressure of a real gas, slowing the molecules and reducing collisions with the walls.

$$.a = \frac{(pressure)(volume)^2}{mole^2} = atm\, L^2\, mol^2$$

$$b = \frac{volume}{mole} = L\, mol^{-1}$$

- The higher the value of *a*, the greater the attraction between molecules and the more easily the gas will compress.
- The *b* term represents the excluded volume of the gas or the volume occupied by the gas particles.

Notice that the van der Waals equation becomes the Ideal Gas Law as these two correction terms approach zero.

Van der Waals equation is valid over a wide range of temperature and pressure. It fails to give the perfect agreement at very high pressure and low temperature. Therefore numerous attempts have been made to modify the Vander Waals equation.

The Vander Waals equation for 1 mole of a gas is given by:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \ldots\ldots..(1)$$

On expanding equation (1)

$$PV + \frac{a}{V} - Pb + \frac{ab}{V^2} - RT = 0 \ldots(2)$$

Multiplying (2) by $\frac{V^2}{P}$

$$\frac{V^2}{P}\left(PV+\frac{a}{V}-Pb+\frac{ab}{V^2}-RT\right)=0$$

$$V^3+\frac{aV}{P}-bV^2-\frac{ab}{P}-\frac{RTV^2}{P}=0\ \ldots\ldots(3)$$

Equation (3) is rearranged in the powers of V

$$V^3-\left(b+\frac{RT}{P}\right)V^2+\frac{aV}{P}-\frac{ab}{P}=0\ \ldots\ldots(4)$$

The above equation (4) is a cubic equation of V, which can have three roots. At the critical point, all the three values of V are equal to the critical volume V_c

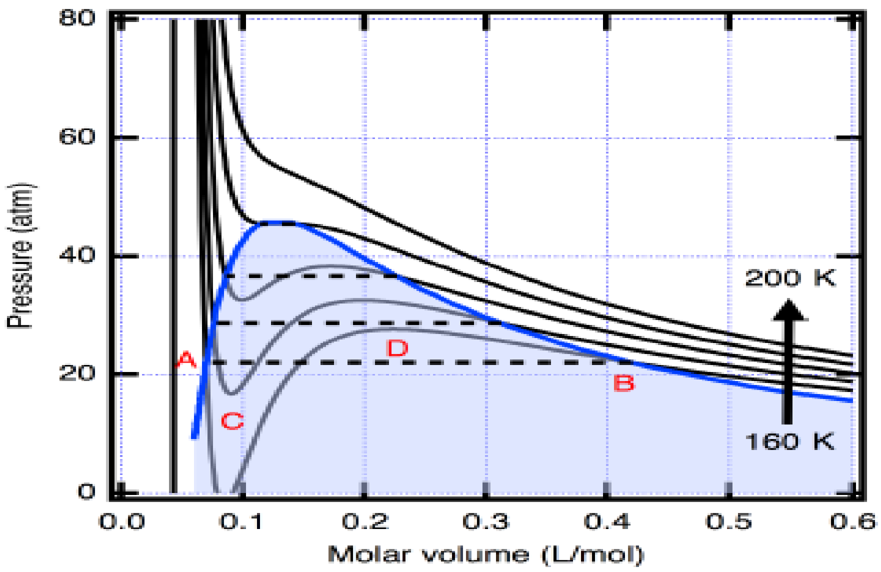


Figure (6): Vander Waals isotherms

The critical condition, in terms of the principle of continuity of the gaseous and liquid phases, can be written as:

$$V^3 = V_c^3$$

$$V^3 - V_c^3 = 0\ \ldots\ldots(5)$$

Expanding Equation (5)

$$V^3-3V_cV^2+(3V_c^2)V-V_c^3=0\ \ldots\ldots(6)$$

Equating the coefficients for the quadratic term V^2 in Equations **(4) and (6):**

$$3V_c = b + \frac{RT_c}{P_c} \ldots\ldots.(7)$$

$$3V_c^2 = \frac{a}{P_c} \ldots\ldots\ldots (8)$$

$$V_c^3 = \frac{ab}{P_c} \ldots\ldots\ldots (9)$$

By dividing equation (8) on (9)

$$V_c = 3b \ldots\ldots.(10)$$

By substituting equation (10) in equation (8)

$$3(9b^2) = \frac{a}{P_c} \rightarrow 27\, b^2 = \frac{a}{P_c}$$

$$P_c = \frac{a}{27\, b^2} \ldots\ldots.. (11)$$

By substituting equations (10) and (11) in equation (7)

$$3 \times 3b = b + \frac{RT_c}{P_c} \times 27b^2$$

$$T_c = \frac{8a}{27Rb} \ldots\ldots (12)$$

Other equations of State

The Virial Equation of state: is a model that attempts to describe the properties of a real gas.The actual behavior is often described with the virial equation:

$$PV = nRT\left(1 + \frac{B}{nV} + \frac{C}{nV^2} + \frac{D}{nV^3} \ldots\ldots\right)$$

Where B, C and D are temperature dependent constant and are called second, third.., etc virial coefficients. The values of these coefficients can be calculated from the experimental P-V-T measurements. In general the coefficient B is negative at low temperature, becoming zero then positive as the temperature increased. The temperature at which B is zero is known as the Boyle temperature, T_B, and it is the temperature at which the repulsive forces between the gas molecules exactly balance the attractive forces between the gas molecules.

$$\boldsymbol{T_B = \frac{a}{Rb} = \frac{27}{8}T_c}$$

The Law of Corresponding States:

An important general technique in science for comparing the properties of objects is to choose a related fundamental property of the same kind and to set up a relative scale on that basis. We have seen that the critical constants are characteristic properties of gases, so it may be that a scale can be set up by using them as yardsticks. We therefore introduce the dimensionless **reduced variables** of a gas by dividing the actual variable by the corresponding critical constant:

$$\frac{P}{P_c} = P_r, \qquad \frac{V}{V_c} = V_r\ , \qquad \frac{T}{T_c} = T_r$$

Van der Waals, who first tried this procedure, hoped that gases confined to the same reduced volume, V_r , at the same reduced temperature, T_r , would exert the same reduced pressure, p_r .

The observation that real gases at the same reduced volume and reduced temperature exert the same reduced pressure is called the **principle of corresponding states**. The principle is only an approximation. It works best for gases composed of spherical molecules; it fails, sometimes badly, when the molecules are non-spherical or polar.

We express Vander Waals equation in terms of the reduced variables, which gives:

$$\left(P_c P_r + \frac{a}{V_c^2 V_r^2}\right)(V_c V_r - b) = RT_c T_r$$

From the critical points equations (10,11,12):

$$\left(P_r\frac{a}{27b^2}+\frac{a}{9V_r^2b^2}\right)(3V_rb-b)=RT_r\frac{8a}{27Rb}$$

$$\frac{a}{27b^2}\left(P_r+\frac{3}{V_r^2}\right)(3V_r-1)b=\frac{8aT_r}{27b}$$

$$\frac{a}{27b}\left(P_r+\frac{3}{V_r^2}\right)(3V_r-1)=\frac{8aT_r}{27b}$$

$$\boldsymbol{\left(P_r+\frac{3}{V_r^2}\right)(3V_r-1)=8T_r}$$

This equation has the same form as the original, but the coefficients *a* and *b*, which differ from gas to gas, have disappeared.

It follows that if the isotherms are plotted in terms of the reduced variables then the same curves are obtained whatever the gas. This is precisely the content of the principle of corresponding states, so the van der Waals equation is compatible with it.

Solved Examples

Example 1: In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas?

$$\frac{P_1V_1}{n_1T_1}=\frac{P_2V_2}{n_2T_2}=R$$

Cancellation of the volumes (because $V_1 = V_2$) and amounts of moles (because $n_1 = n_2$) on each side of the combined gas law results in:

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

$$P_2=\frac{T_2}{T_1}\times P_1$$

$$P_2=\frac{500\ K}{300\ K}\times 100\ atm=167\ atm$$

Example 2: Calculate the volume of 1.2 kg an ideal gas with a molar mass of 55 g/mol at a pressure of 120 kPa, and a temperature of 80°C. Also, what is the density of the gas?

$$w=1.2\ kg\ \times 1000=1200\ g$$

$$M = 55\ g/mol$$

$$P = 120kpa\ \times \frac{1}{101.325} = 1.184\ atm$$

$$T = 80 + 273.15 = 353.15\ K$$

$$M = \frac{wRT}{PV}$$

$$V = \frac{wRT}{PM} = \frac{1200\ g\ \times 0.08206\ \frac{L.atm}{mol.K} \times 353.15\ K}{1.184\ atm\ \times 55\ g/mol} = \frac{34775.4}{65.12}$$
$$= 534.02\ \mathrm{L}$$

$$M = \frac{\rho RT}{P}$$

$$\rho = \frac{PM}{RT} = \frac{1.184\ atm\ \times \frac{55}{1000}\ kg/mol}{0.08206\ \frac{L.atm}{mol.K} \times 353.15\ K} = \frac{0.06512}{28.979} = 2.25\ \frac{kg}{L}$$

Example 3: The compressibility factor **Z**= $\frac{PV}{nRT}$ for CO_2 at 273 K and 100 atm (101.325 x 10^5 Nm^{-2}) is 0.2007. Calculate the volume occupied by 0.1 mole of the gas at 100 atm and 273K (a) by the ideal gas equation (b) by making use of the compressibility factor.

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{(0.1\ mol)\left(0.08206\frac{L.atm}{mol.K}\right)(\ 273\ K)}{100\ atm} = 0.0224L$$

$$\mathbf{Z} = \frac{PV}{nRT}$$

$$V = \frac{Z\ nRT}{P} = \frac{(0.2007)(0.1\ mol)(0.08206\frac{L.atm}{mol.K})(273K)}{100\ atm}$$
$$= 4.498 \times 10^{-3}\ L$$

Example 4: Calculate the pressure in atm. Exerted by 2 moles of chlorobenzen vapours confined to 10 L vessel at 298K using:

(a) The ideal gas equation (b) the Vander Waals equation

a= 25.43 L^2 atm mol^{-2} , b= 0.1453 L mol^{-1}

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{(2\ mol)\left(0.08206\frac{L.atm}{mol.K}\right)(\ 298\ K)}{10\ L} = 4.89\ atm$$

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

$$= \frac{(2\ mol)\left(0.08206\frac{L.atm}{mol.K}\right)(\ 298\ K)}{10 - (2 \times 0.1453)} - \frac{25.43\ \times 2^2}{10^2}$$

$$P = \frac{48.9316}{9.7694} - \frac{101.72}{100} = 5.0396 - 1.0172 = 4.0224\ atm$$

Example 5: The Vander Waals constants for gaseous HCl are:

a= 0.367 N.m^4. mol^{-2} , b= 0.0408 x 10^{-3} m^3 mol^{-1} , calculate the critical points.

$$V_c = 3b = 3(0.0408\ \times 10^{-3}\ m^3 mol^{-1})$$

$$\boldsymbol{P_c = \frac{a}{27\ b^2}} = \frac{0.367\ N\ m^4 mol^{-2}}{27(0.048\ \times\ 10^{-3} m^3 mol^{-1})^2} = 8.1 \times 10^6\ N\ m^{-2}$$

$$T_c = \frac{8a}{27Rb} = \frac{8\ (0.367\ N\ m^4 mol^{-2})}{27(8.314\ N\ m\ K^{-1} mol^{-1})(0.0408\ \times 10^{-3}\ m^3 mol^{-1})}$$
$$= 321K$$

Exercises:

1- A perfect gas undergoes isothermal compression, which reduces its volume by 2.20 dm^3. The final pressure and volume of the gas are 5.04

bar and 4.65 dm^3, respectively. Calculate the original pressure of the gas in (a) bar, (b) atm.

2- A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23°C. What can its pressure is expected to be when the temperature is 11°C?

3- Could 25 g of argon gas in a vessel of volume 1.5 dm^3 exert a pressure of 2.0 bar at 30°C if it behaved as a perfect gas? If not, what pressure would it exert? (b) What pressure would it exert if it behaved as a van der Waals gas?

4- A sample of 255 mg of neon occupies 3.00 dm^3 at 122 K. Use the perfect gas law to calculate the pressure of the gas.

5- At 500°C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m^{-3}. What is the molecular formula of sulfur under these conditions?

6- Calculate the pressure exerted by 1.0 mol H_2S behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at 273.15 K in 22.414 dm^3, (ii) at 500 K in 150 cm^3.

7- A certain gas obeys the van der Waals equation with $a = 0.76\ m^6\ Pa\ mol^{-2}$.

Its volume is found to be $4.00 \times 10^{-4}\ m^3\ mol^{-1}$ at 288 K and 4.0 MPa. From this information calculate the van der Waals constant b.

What will be the volume of a gas when 3 liters of it cooled down from 15 C to -73 C at constant pressure?