

Physical Pharmacy



Behavior of

Gases

Contents

In this lecture you will learn:

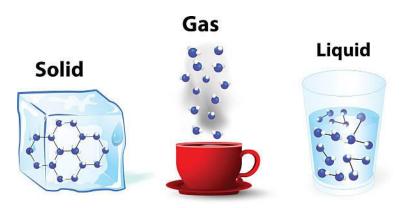
- What is Gas and what are the properties of Gases?
- Gas Laws and ideal gas equation:
 - How to calculate M. wt of gas using ideal gas equation?

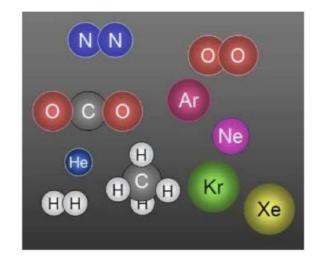
- Ideal and Real Gas: what are the differences?
- Van der Waals modified gas equation (for real gases)
- Liquefaction of Gases:
 - What does it mean and how to achieve it?
 - Aerosols as an example for gas liquefaction



What is Gas?

- Gas is one of the fundamental states of matter.
- A pure gas may be made up of:
- 1) Individual atoms (inert gases)
- Elemental molecules (made from one type of atom, e.g., N2 gas
- 3) Compound molecules made from a variety of atoms.







What is Gas?

The Atmosphere is all around us

→ an "ocean" of gases mixed together

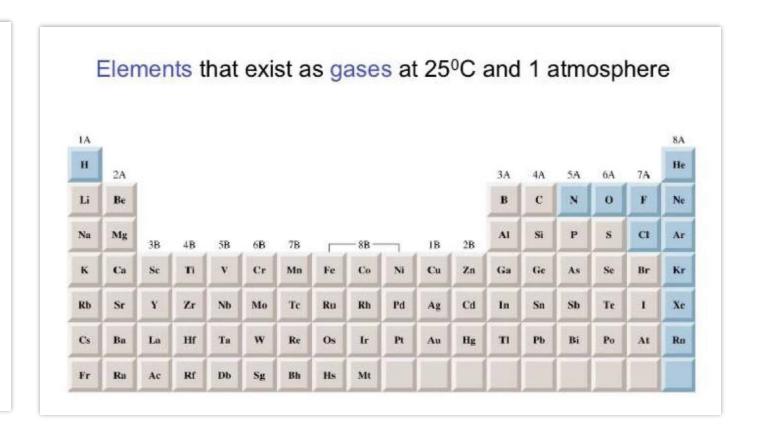


Composition

nitrogen (N ₂)	~78%
oxygen (O ₂)	~21%
argon (Ar)	~1%
carbon dioxide (CO ₂)	~0.04%
water vapor (H ₂ O)	~0.1%

Trace amounts of:

He, Ne, Rn, SO₂, CH₄, N_xO_x, etc.





Properties of Gases

- Compared to other states of matter:
- 1. Gases have negligible intermolecular forces between its particles, and gas particles move at high velocity and are separated by large distances.
- 2. Gases show the most uniform behavior irrespective of the nature of the gas and have the following properties:
 - a) They expand indefinitely and fill up the whole vessel in which they are placed.
 - b) They can be compressed by the application of pressure.
 - c) They can be liquefied by cooling and applying pressure.
 - d) 'They possess low densities under ordinary conditions of temperature and pressure.
 - e) They intermix spontaneously, i.e., they show the property of diffusion.
 - f) They exert pressure on the walls of the vessel in which they are contained.



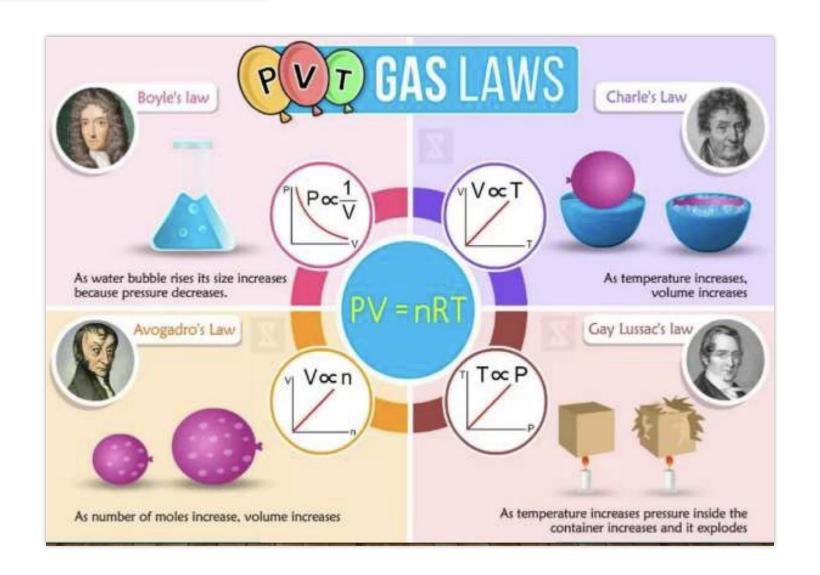
Measurable Properties of Gases

- [P = Pressure of gas in atmospheres (atm)
- V = Volume of gas in liters (L)
- n = Number of moles of gas in moles (mol)
- **T** = Temperature of gas in Kelvin (K)
- R = Ideal Gas Constant 0.082057

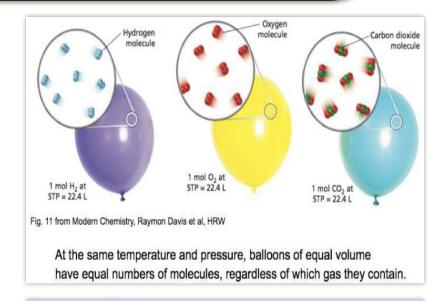
 Mol-k

Units of pressure: since pressure is force /area so: dyne/cm2, or 1 atm = 760 torr = 760 mmH = 1×10^5 Pa = 14.69 psi = 101.325 kPa 1 L = 1000 mL = 1000 Cm³ zero °C = 273 Kelvin, so: degree in K = °C+ 273

















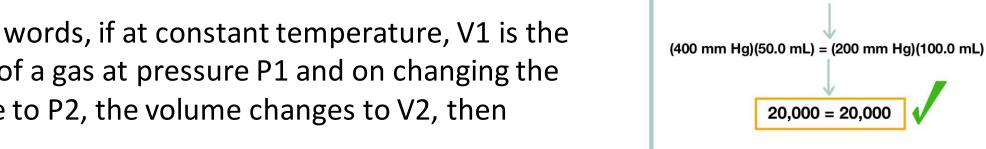
P1xV1=P2xV2

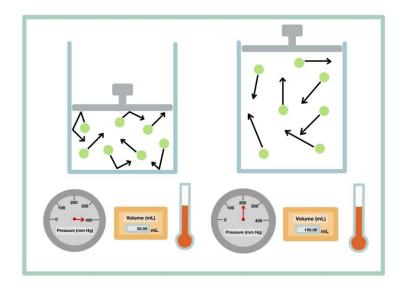
1- Boyle's law

- The volume of a given mass of a gas is inversely proportional to its pressure with temperature remaining constant.
- Mathematically, if V is the volume of a gas at pressure P, and if temperature is kept constant, then:

$$P= 1/v \text{ or } PV = k$$

In other words, if at constant temperature, V1 is the volume of a gas at pressure P1 and on changing the pressure to P2, the volume changes to V2, then



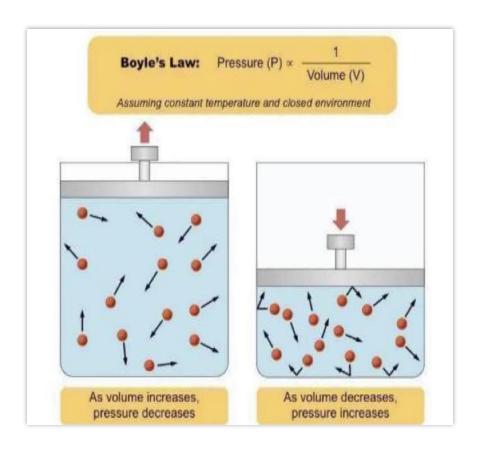


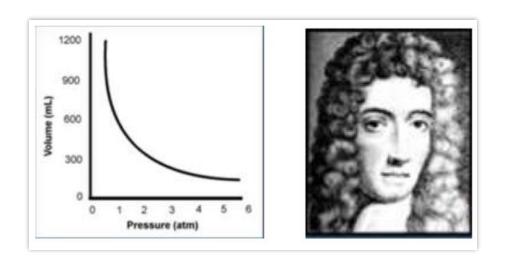
Boyle's Law:

 $P_1V_1 = P_2V_2$



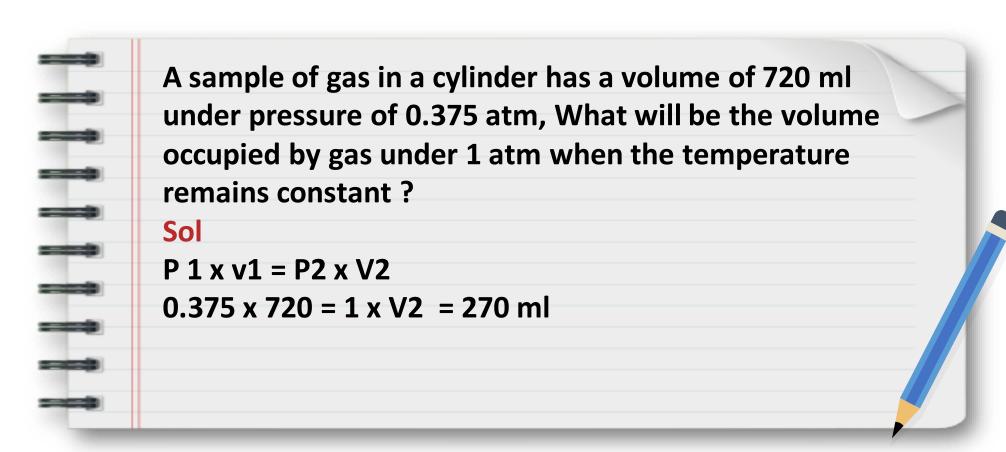
1- Boyle's law





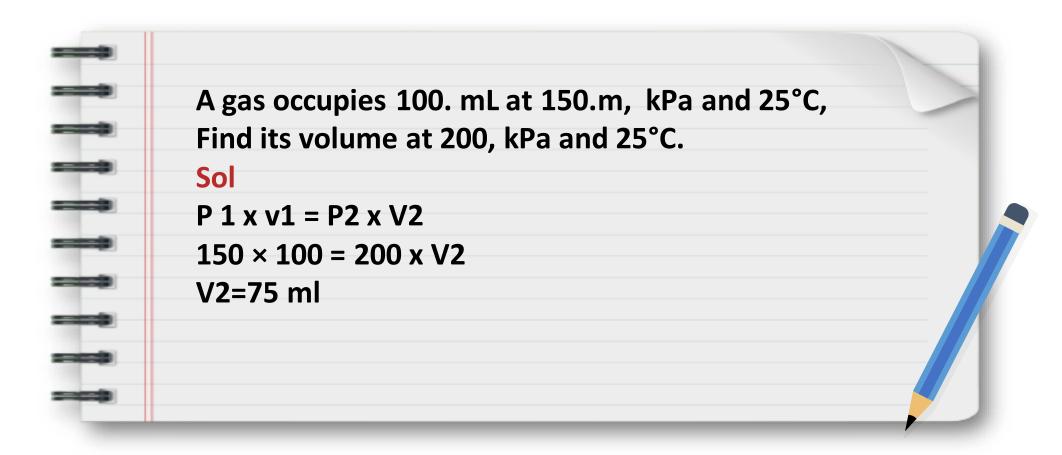


1- Boyle's law: Examples



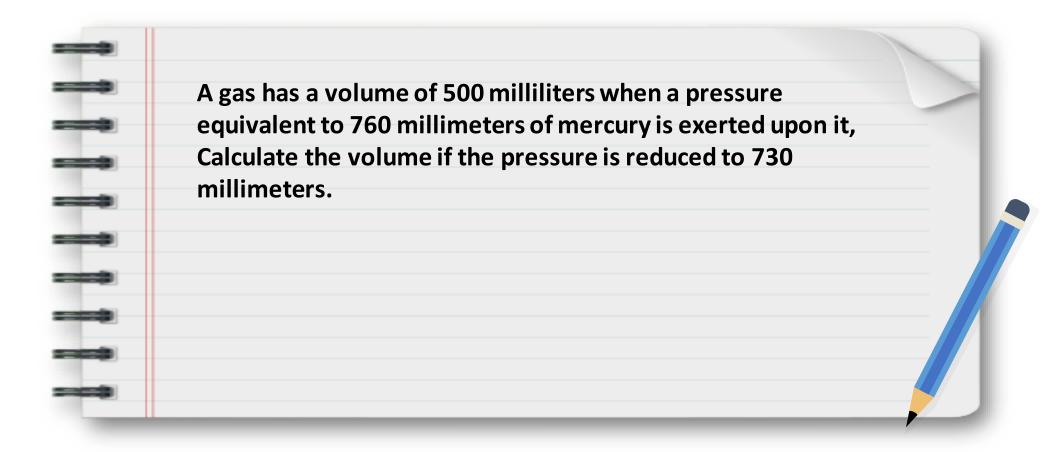


1- Boyle's law: Examples





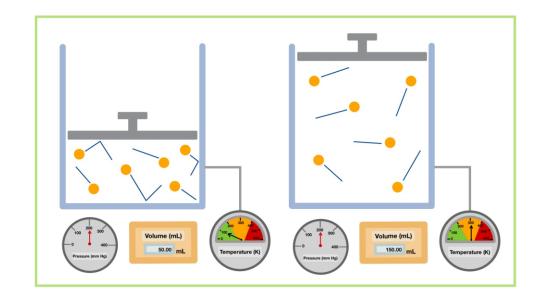
1- Boyle's law: Exercise:





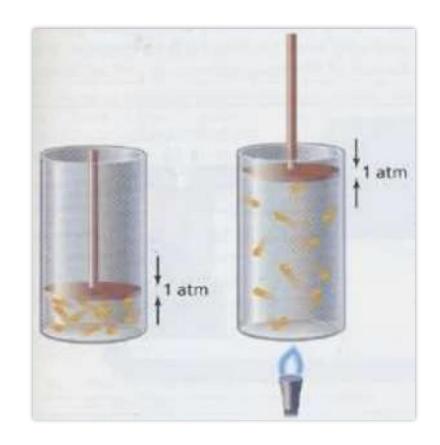
2- Charles law

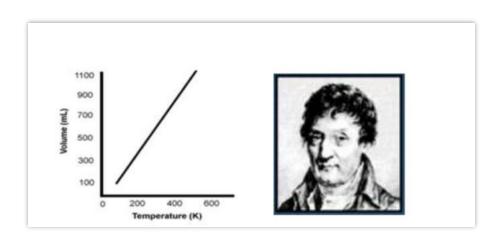
- The volume of a given mass of a gas is directly proportional with temperature at constant pressure V∞T, V =kT
- Or V/T =K or V1/T1 = V2/T2
- **Temperature must be in Kelvin units**





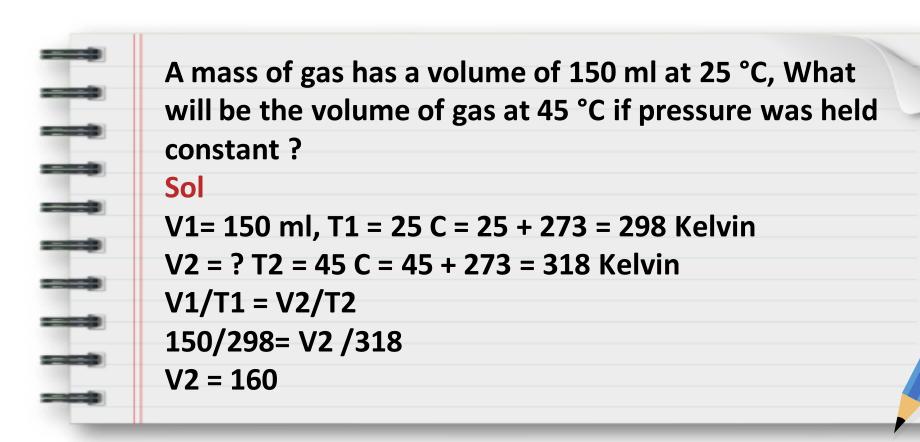
2- Charles law





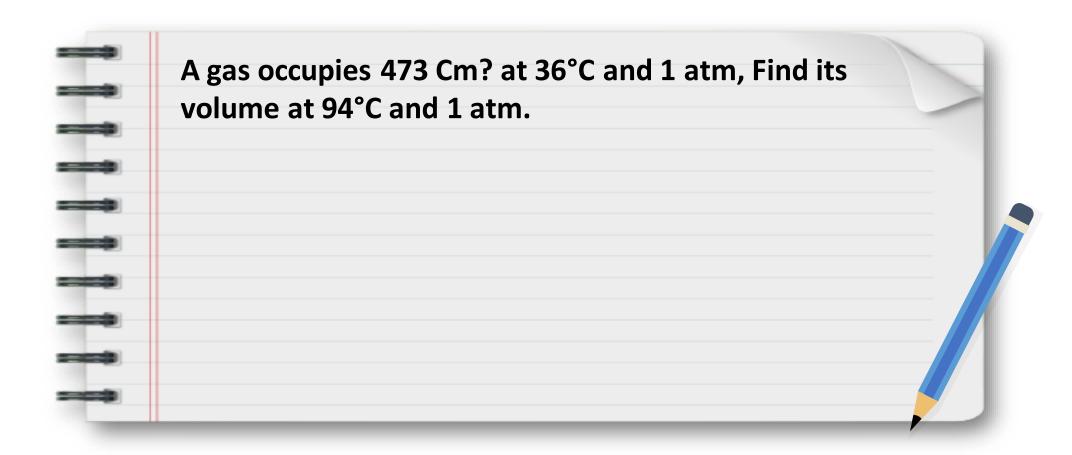


2- Charles law: Examples





2- Charles law: Exercise





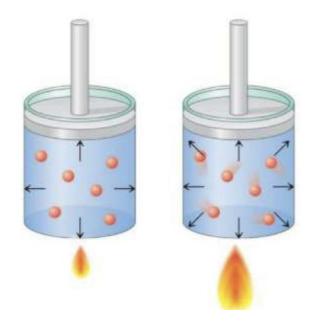
3- Gay-Lussac's law

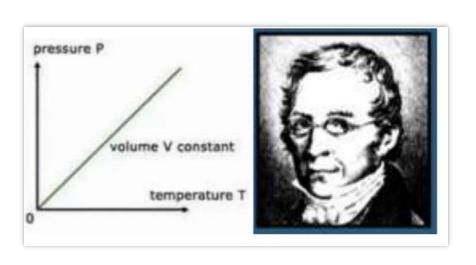
- The pressure of a given mass of a gas is directly proportional with temperature at constant volume
- P1/T1=P2/T2
- **Temperature must be in Kelvin units**
- Should you throw an aerosol can into a fire? What could happen?

Remember: increasing the temperature gets the particles moving faster causing an increase in the number and energy involved in collisions; thus an increase in pressure



3- Gay-Lussac's law







4- Avogadro's Law

- The volume of a gas is directly proportional to the number of moles present in the gas if temperature and pressure are kept constant.
- In other words: Under similar conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.
- Or: 1 mole (n) of the substance (gas, liquid, or solid) contains the same number of molecules regardless of the substance identity.
- This number is known as Avogadro's number and is equal to (6.023×10^{23}) .

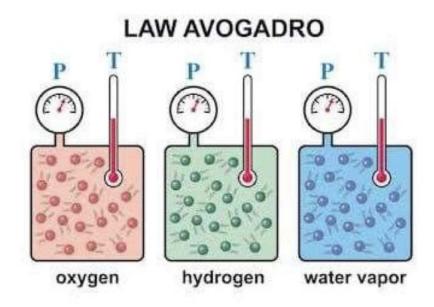
$$V \propto n$$

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

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



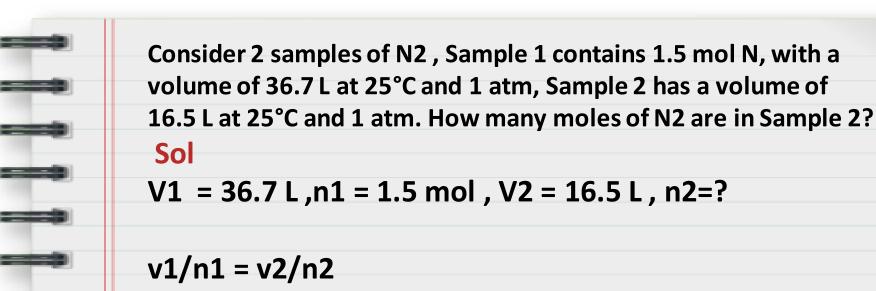
4- Avogadro's Law







4- Avogadro's Law: Example

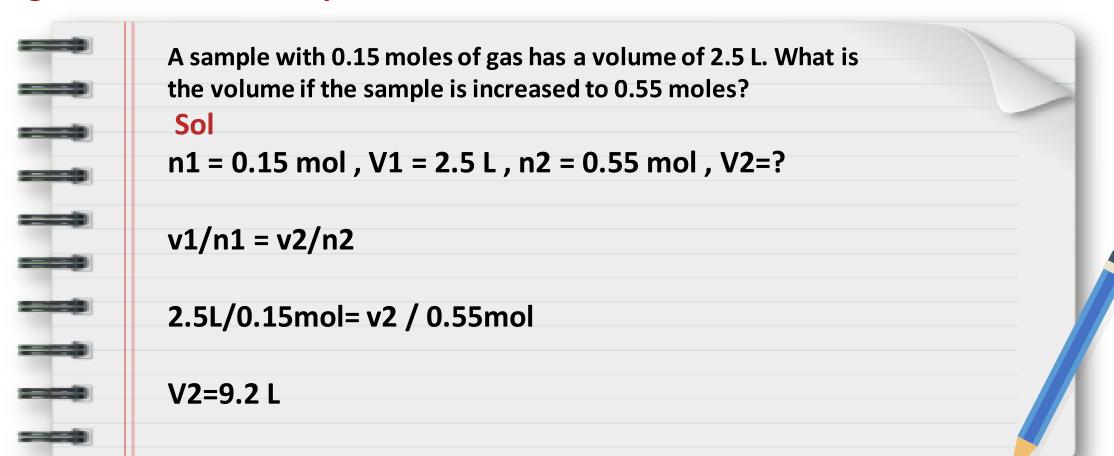


$$v1/n1 = v2/n2$$

$$n2 = 0.67 \text{ mol}$$

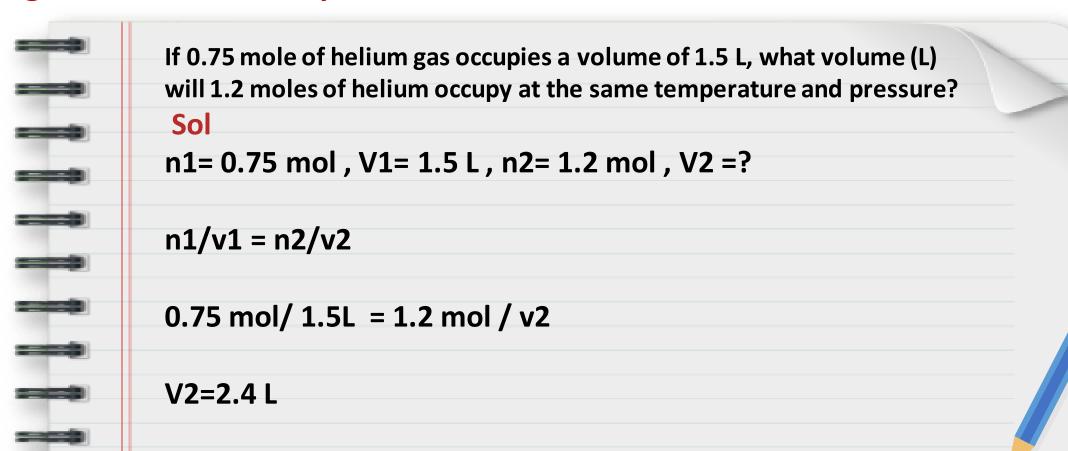


4- Avogadro's Law: Example





4- Avogadro's Law: Example





The Combined Gas Law Equation: (the Ideal Gas Equation)

- The previously mentioned laws and related equations may be combined to give a general equation, called the gas equation (or more correctly, ideal gas equation: since real gases do not follow this equation)
- Mathematically, ideal gas equation is given by: PV / T = R

P= pressure

V = volume

n = amount of substance

R = ideal gas constant

T = temperature

n= wt (gm)/M.wt (molar)



The Combined Gas Law Equation: (the Ideal Gas Equation)

Under one set of conditions, although P, V and T change, the ratio P/T is constant and can be represented as: PV = RT

R is a constant value: the gas constant

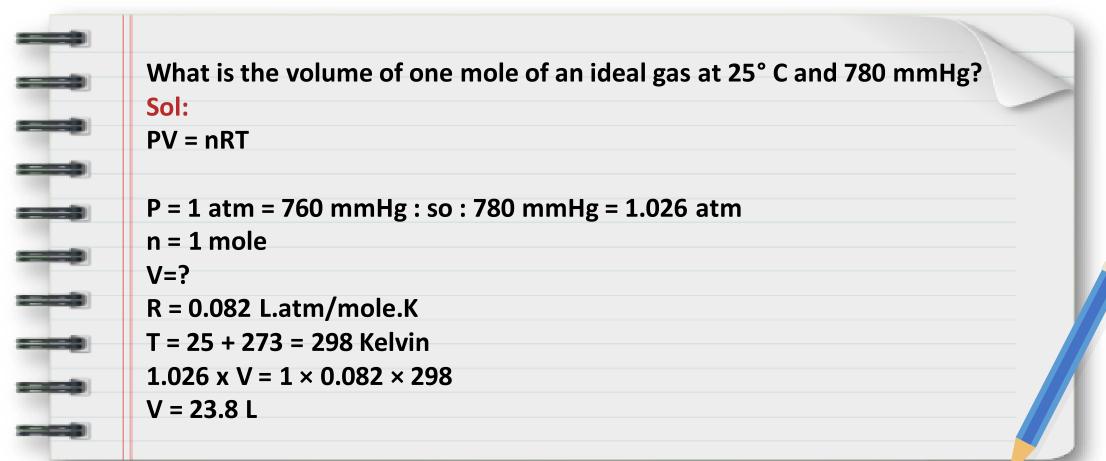
This equation is correct for 1 mole (i.e., g molecular weight) of gas: for n moles it becomes: PV = nRT V∞1/P (Boyle's law)

V∞T (Charles's law)

V∞n (Avogadro's law)

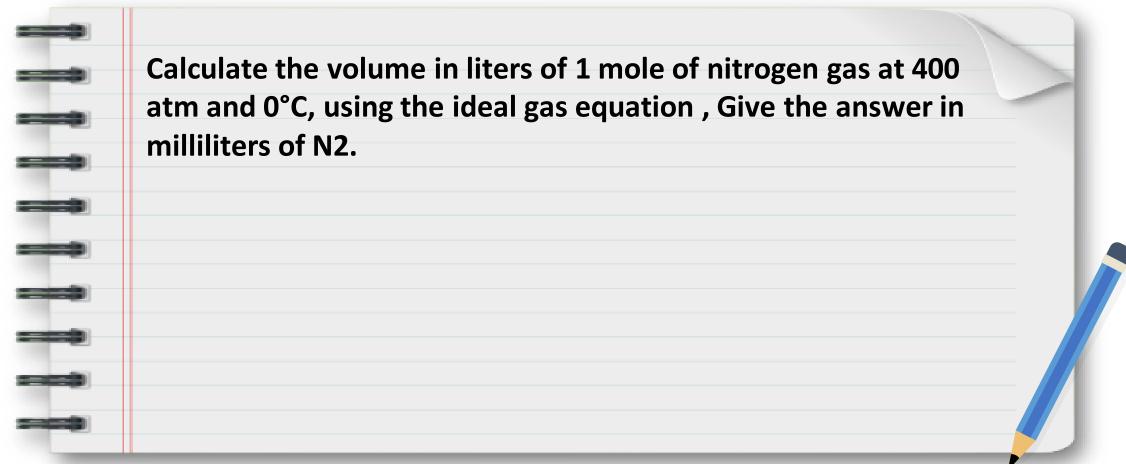


The Combined Gas Law Equation (the Ideal Gas Equation): Example





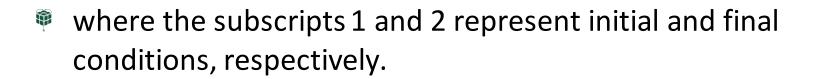
The Combined Gas Law Equation (the Ideal Gas Equation): Exercises

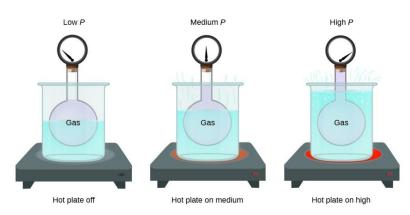




The Combined Gas Law Equation: (the Ideal Gas Equation)

Ideal gas law for 2 set of condition is:





- In this form of the gas constant R does not appear.
 - When working with this equation you may use any units which are convenient for **P** and **V**, but **T** must be in Kelvin

The Combined Gas Law Equation (the Ideal Gas Equation): Example



What is the volume of a weather balloon rising 2 miles into the upper atmosphere at atmospheric pressure of 8.77×10^3 atm, and temperature of -44.7 °C, if you know that it has initial volume of 2.5 L at ground level at 1 atm pressure and 24 °C and 780 mmHg.

Sol

$$\frac{P1V1}{T1} = \frac{P2V2}{T2}$$

$$1x2.5 / 297 = 8.87x10^{-3}v2 / 228.3$$

$$V2=219.6 L$$



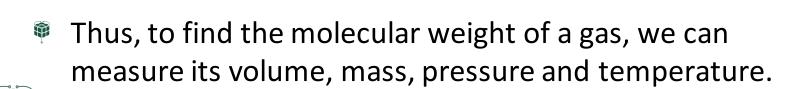
How do you calculate molecular weight of a gas?

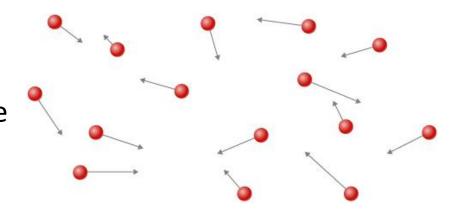
To find the molecular mass of a gas, we can assume it behaves ideally and use the ideal gas law

$$Pv = nRT$$

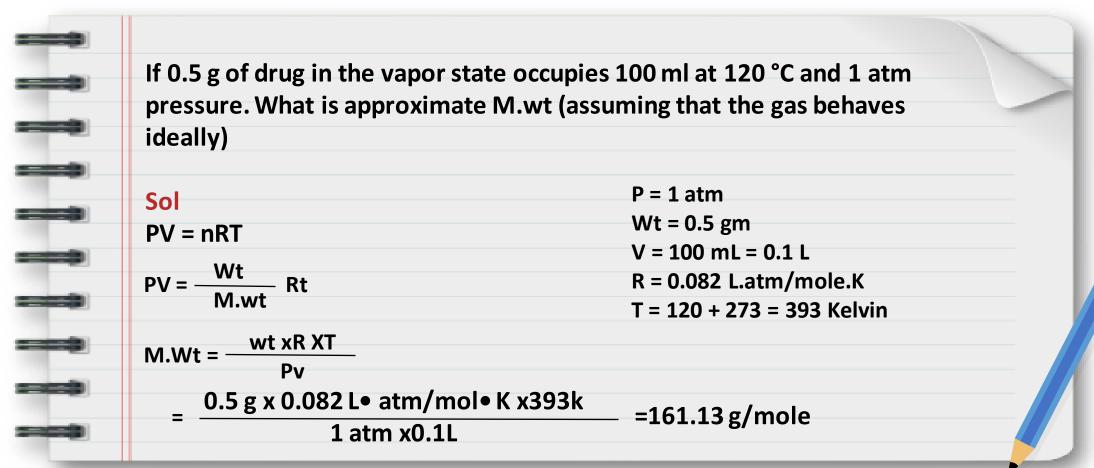
We can modify this law in by replacing the number of moles of gas (n) by its equivalent g/M, in which g is the mass (m) and M is molecular weight of the gas:

$$Pv = \frac{g}{M} RT$$





How do you calculate molecular weight of a gas? : Example





Numerical values of the R in various units

- The gas constant (R) appears in the equation of ideal gas law as well as many other equations in many fields.
- Therefore, its value and units varies depending on the equation used as follows:

$$PV = nRT$$

$$R = \frac{P \times V}{n \times T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{temperature K}}$$

$$R = \frac{\frac{\text{Force}}{\text{Area}} \times (\text{Length})^3}{\text{Moles} \times \text{Degrees}} = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Moles} \times \text{Degrees}}$$

$$R = \frac{\text{Force} \times \text{Length}}{\text{Moles} \times \text{Degrees}} = \frac{\text{Work}}{\text{Moles} \times \text{Degrees}}$$

Units	Numerical Value	Used in gas laws
L-atm/mol-K	0.08206	gas laws
J/mol-K	8.314	
cal/mol-K	1.987	
m³-Pa/mol-K	8.314	
L-torr/mol-K	62.36	Used in
		thermodynamics



R = Work done per degree per mole.

Numerical values of the R in various units

1. At STP conditions : P= 1 atm, V = 22.4 1 , T= 273 k , n = 1 mole

$$R = \frac{pv}{nt} = \frac{1x\ 22.4}{1x\ 273}$$

 $R = 82.1 \text{ ml atm } K^{-1} \text{mol}^{-1}$

- =0.08206 L.atm/mol.K
- 2. At units of energy:

P=1 atm = $1.0133 \times 10^6 \text{dyne/cm}^2$, V =22.414, L = 22414 CM³, T= 273 K, n = 1 mole

$$R = \frac{pv}{nt} = R = \frac{1.0133x10^6 \frac{dyne}{cm^2} x 22414cm^3}{1mole x 273 k} = 8.314^7 dyne \frac{cm}{Mole x k}$$

8.314 x 10⁷ erg/mole. K = 8.314 Joules/mole.K (since 1 Joule = 10⁷ erg, and erge = dyne × cm)

Numerical values of the R in various units

 \mathfrak{P} 3. For expressing in SI units, put 10^7 erg = 1 J

$$R = \frac{8.314 \times 10^7}{10^7} Joules \deg^{-1} mol^{-1}$$

 $=8.314JK^{-1}mol^{-1}$

4. Further putting 4.184 J = 1 calorie, we have

$$R = \frac{8.314}{4.184}$$

 $1.987 = 2 \text{ cal } \text{K}^{-1} \text{ mol}^{-1}$



Standard temperature and pressure (STP)

- As the volume of a given mass of gas differs with temperature and pressure, the STP conditions are used as a reference point to compare gases.
- It refers to the nominal conditions in the atmosphere at sea level.

Standard molar volume

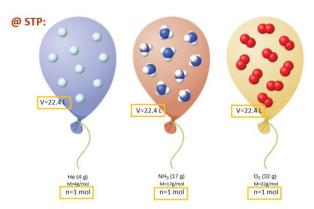
- (also called, molar volume) is the volume of 1 mole of gas at STP.
- For ideal gas : Pv = nRT
 V = nRT/PV
 = (1)(0.082)(273)/(1)



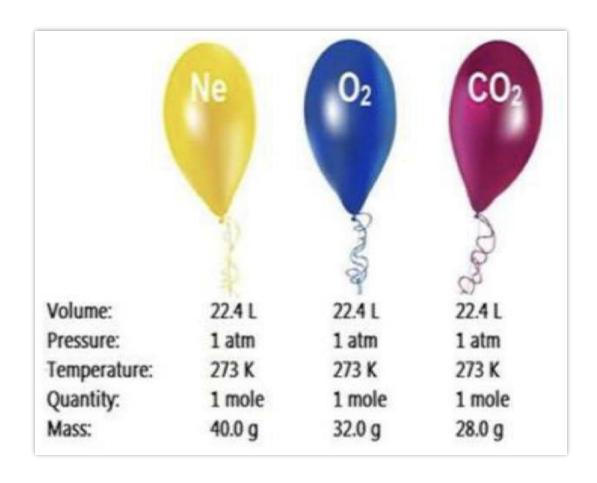


Standard Temperature & Pressure

0°C 273 K - OR -101.325 kPa 760 mm Hg



An overview on Gas Laws

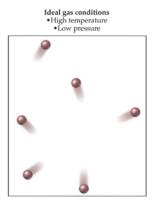


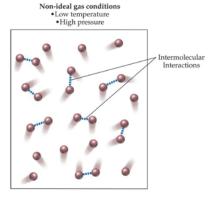


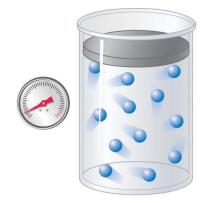
Ideal Gases

- The properties of matter in gaseous state can be described by the ideal gas law.
- The ideal gas law is derived from a combination of gas laws formulated by Boyle, Charles, and Gay-Lussac.
- The ideal gas obeys the following ideal gas equation: Pv = nRT

Ideal vs. Real Gases











(b) High pressure



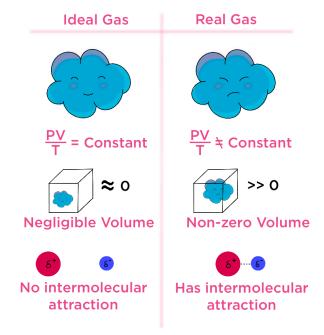
An overview on Gas Laws

Ideal Gases

- The ideal gas equation describes the behavior of an ideal gas as a function of :
 - temperature, pressure, volume, and amount of gas.
- An ideal gas is a is only hypothetical (i.e., an imaginary gas)

Ideal gases are only "ideal" when the particles of which they are composed "act independently".

Differences Between Real and Ideal Gases

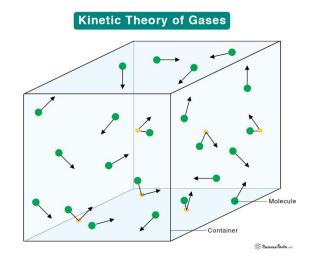


At low temperature or high pressure, real gas behaves differently, but at standard temperature and pressure, real gas behaves similar to ideal gas



The main assumptions in the ideal gas law derivation (known as kinetic molecular theory (KMT)) are

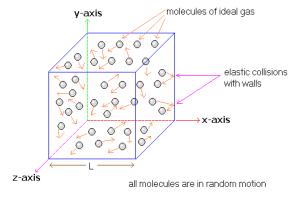
- 1. The gas molecules are very small, hard spheres with no intermolecular interactions between the molecules (i.e., force of attraction between gas molecules is zero)
- 2. The particles take up no space (have no molecular volume: the volume occupied by the molecules is negligible in comparison to the total volume of the gas)



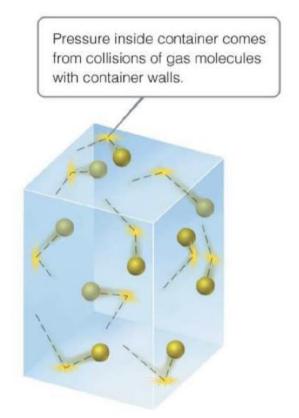


The main assumptions in the ideal gas law derivation (known as kinetic molecular theory (KMT)) are

- 3. The particles are in state of random, constant rapid motion and collisions between the molecules are perfectly elastic (i.e., there is no energy loss when molecules collide with one another or with the walls of the vessel), and the force of collision will depend only on the particle mass and velocity.
- 4. The average kinetic energy of a molecule is directly proportional to the absolute temperature of gas.
- a) All gases at the same temperature have the same average kinetic energy.



Van der Waals realized that two of the assumptions of the kinetic molecular theory were questionable!!

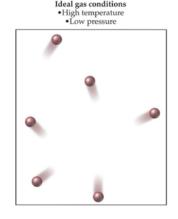


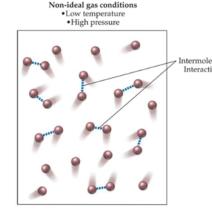


Real Gases

- In reality, all gases are real gases and show deviation from ideal behavior.
- Real gases obey the gas laws to a fair degree of approximation only at low pressures and high temperatures
- In reality, there is a small force of attraction between gas molecules that tends to hold the molecules together
- This force of attraction has two consequences:
- 1. Gases condense to form liquids at low temperatures (liquefaction of gases: to be explained later)
- 2. the pressure of a real gas is sometimes smaller than expected for an ideal gas (to be explained later)

Ideal vs. Real Gases





Differences Between Real and Ideal Gases

Real Gases

- Real gases obey gas laws only at low pressures and high temperature.
- The volume occupied , by the molecules is not negligible as compared to the total volume of the gas.
- The force of attraction are not negligible at all temperatures and pressures.
- If the gas is compressed or cooled,

Ideal gases

- Ideal gases obey all gas laws under all conditions of temperature and pressure.
- The volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.
- The force of attraction among the molecules are negligible.
- Particles in their movement will hit the wall with a force which depends only on the particle mass and velocity.
- The gas can be compressed or cooled without being liquified



DEVIATIONS OF REAL GASES FROM GAS LAWS (Deviations from ideal behavior)

Real gases deviate significantly from ideal gas behavior at low temperatures or high pressures

Effect of low temperature for real gases

- The assumption that there is no force of attraction between gas particles cannot be true. (see assumption 1 in the kinetic molecular theory)
- As temperature decreases, the average kinetic energy of the gas particles decreases.
- A larger proportion of gas molecules therefore have insufficient kinetic energy to overcome attractive intermolecular forces from neighboring atoms.



Effect of low temperature for real gases

- The attraction forces between the particles will pull the particles which hit the wall of the container back toward the center of the container, this will slow down the particles and means that gas molecules become "stickier" to each other, and collide with the walls of the container with less frequency and force, decreasing pressure of real gas below that of ideal values.
- In conclusion, at low temperatures: The pressure of a real gas is sometimes smaller than expected for an ideal gas (P real < P ideal)</p>



DEVIATIONS OF REAL GASES FROM GAS LAWS (Deviations from ideal behavior)

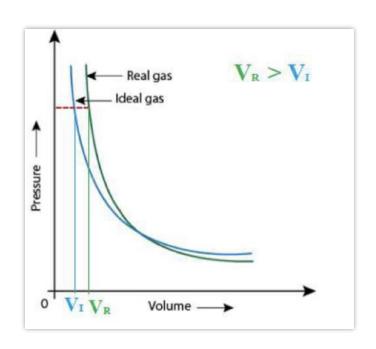
Real gases deviate significantly from ideal gas behavior at low temperatures or high pressures

Effect of high pressure

- For ideal gases we know that $V \approx 1/P$ It means that increasing the pressure reduces the volume of gas
- But: The assumption that gas particles occupy no volume is not true (see assumption 2 in the kinetic molecular theory)
- Real gas particles occupy a fraction of the total volume of the gas and this fraction is not negligible as compared to total volume of the gas.

Effect of high pressure

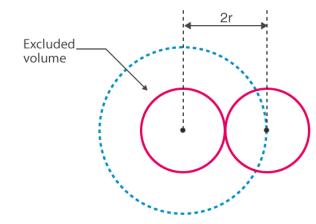
- Therefore "Real gases" are not as compressible at high pressures as an "ideal gas".
- In conclusion, at high pressure, The volume of a Real gases is therefore larger than expected for Ideal gases which is predicted from the ideal gas equation. (V real > V ideal)





VAN DER WAALS' EQUATION (REDUCED EQUATION OF STATE) (EQUATION OF STATE FOR REAL GASES)

Since real gas are composed of gas particles which attract each other, and are therefore influenced by the number of these particles, Van der Waals deduced a modified gas equation by making volume and pressure corrections to the gas equation



Therefore, the van der Waals' equation for n moles of a gas will be :

$$\left(p+\frac{n^2a}{V^2}\right)(v-nb)=nRt$$





a = depends on the strength of attractive forces

VAN DER WAALS' EQUATION (REDUCED EQUATION OF STATE) (EQUATION OF STATE FOR REAL GASES)

- The units for van der Waals' constants a and b depend on the units in which P and V are expressed.
- The gases such as CO2, NH3 and HCl, which can be easily liquefied, have high values of van der Waals' constant a and b and show maximum departure from the ideal gas equation.



Table 1.1 Van der Waals' constants for some common gases:

Gas	atm. L² mol ⁻²	atm. L mol ⁻¹	
H2	0.024 0.0266		
He	0.034	0.237	
Ne	0.21	0.0171	
02	1.36	0.0318	
N2	1.39	0.0391	
Co2	3.59	0.0427	
Hcl	3.67	0.0408	
NH3	4.17	0.0371	
SO2	6.71	0.0564	



Example



Using van der Walls' equation, calculate the pressure exerted by one mole of carbon dioxide. When it occupies a volume of 0.051 at 100 C, given that

a = 3.592, b= 0.0426 and R= 0.0821

1 atm/degree mole.

Sol

It is given that, n = one mole, van der Waals' equation, for one mole $P = \frac{0.0821x373}{0.05-0.0426} - \frac{3.592}{0.0025} = 2701.5 atm$

$$P = \frac{0.0821x373}{0.05 - 0.0426} - \frac{3.592}{0.0025} = 2701.5atm$$

$$a = 3.592$$
 atm 1/Mole $^{-2}$,

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

$$P + \frac{a}{V^2} = \frac{RT}{V - b}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

Substituting the values of a, b, V and Tin the van der Waals' equation,



PHASE CHANGES:

- Condensation: Gas Liquid
- Melting: Solid → Liquid
- Freezing: Liquid → Solid
- ¶ Sublimation: Solid → Gas
- The understanding of the phase diagram is important since the liquefaction of gases involves the physical conversion of matter.

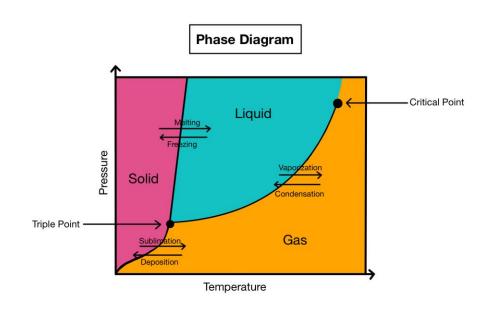
CHANGING STATES OF MATTER





Phase diagram: an overview

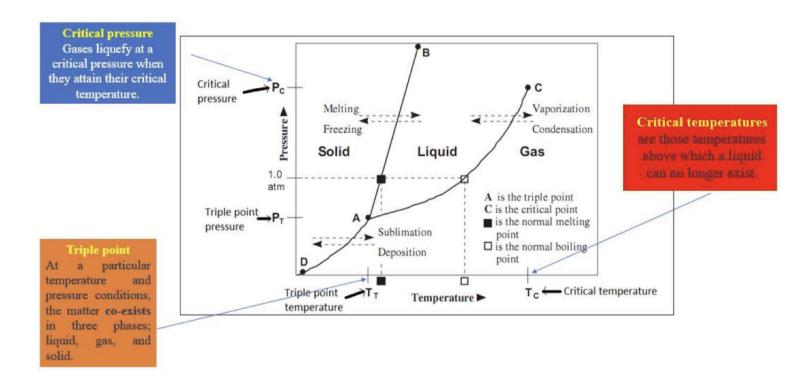
- Every matter exists in a different physical state at different temperature and pressure conditions.
- A phase diagram is a type of chart used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium.
- A typical phase diagram has pressure on the y-axis and temperature on the x-axis.





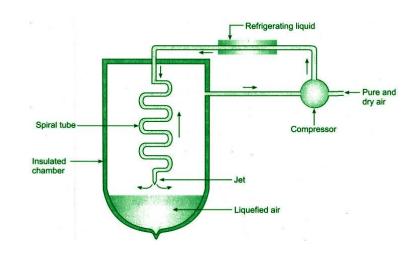
Phase diagram: an overview

- As we cross the lines or curves on the phase diagram, a phase change occurs.
- The diagram is divided into three areas, which represent the solid, liquid, and gaseous states of the substance.





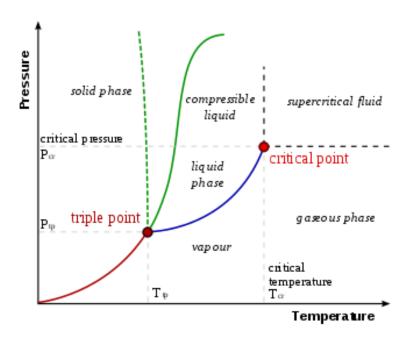
- Liquefaction is the transformation of a gaseous substance into a liquid condition.
- To liquefy a gas, the molecules must be brought closer together.
- Conditions Necessary for Liquefaction of Gases The following are two conditions that must be met in order for gases to be liquefied:
- Low temperature: temperature of gas must be below certain temperature so as to be liquified
- High pressure: the gas must be under certain pressure, above which it can be liquified



When gases are cooled, they lose their kinetic energy and velocity

a. Effect of temperature: Critical Temperature (T)

- No matter how high the pressure applied, each gas has a specific temperature above which it cannot liquefy.
- This temperature is referred to as the gas's critical temperature. It is possible to define it as follows:



The critical temperature of a gas is the temperature above which it is impossible to liquefy it with any amount of pressure.



- A gas must be cooled below its Critical Temperature before it can be liquified.
- For example, Carbon dioxide has a critical temperature of **30.98 C.**
- This means that we need to cool it below 30.98 C in order to liquify it.
- Liquefaction of gases do not occur at temperatures above the critical temperature ?

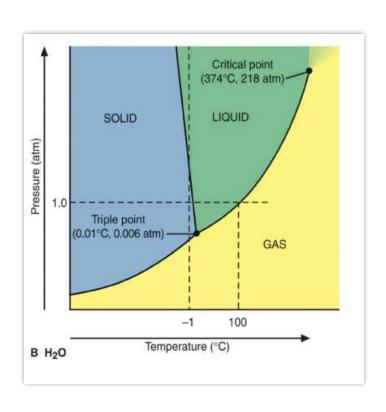
At temperature above the critical temperature value, the molecules have sufficient kinetic energy so that no amount of pressure can bring them within the range of attraction forces that causes the particles to stick together



- If pressure is applied to a gas, the molecules are brought within the range of van der Waals forces and pass into the liquid state.
- Because of these forces, liquids are considerably denser than gases and occupy a definite volume

Effect of pressure: Critical pressure (Pc)

The critical pressure of a gas is the minimal pressure required to liquefy it at the critical temperature





Effect of pressure: Critical pressure (Pc)

The critical temperature serves as a rough measure of the attractive forces between molecules because at temperatures above the critical value, the molecules possess sufficient kinetic energy so that no amount of pressure can bring them within the range of attractive forces that cause the atoms or molecules to "stick" together.

	Water	Helium	
Critical Temperature	647 K	5.2 K	
Critical Pressure	218 atm	2.26 atm	
	The high critical values for water result from the strong dipolar forces between the molecules and particularly the hydrogen bonding that exists	only the weak London force attracts helium molecules, and, consequently, this element must be cooled to the extremely low temperature of 5.2 K before it can be liquefied. Above this critical temperature, helium remains a gas no matter what the pressure.	



Exercise:

The following gases have the given Critical temperature and Critical Pressure values, which gas easier to liquify?

	CO2	Helium	Nitrogen
Critical Temperature	304 K	5.2 K	126 K
Critical Pressure	72.9 atm	2.26 atm	33.5 atm



Aerosols

- Aerosols are pharmaceutical preparations in which the drug is dissolved or suspended in a propellant.
- Aerosols depend in their action on the concept of gas liquefaction and the reversible change of state.
- Aerosol = Propellant gas + drug solution or suspension
- Propellant gas is a material that is liquid under the pressure conditions existing inside the container but that forms a gas under normal atmospheric conditions



Aerosols

- Gases can be liquefied under high pressures in a closed chamber as long as the chamber is maintained below the critical temperature.
- When the pressure is reduced, the molecules expand and the liquid reverts to a gas.
- The container is so designed that, by depressing a valve, some of the drug-propellant mixture is expelled owing to the excess pressure inside the container.
- the drug is nonvolatile, it forms a fine spray as it leaves the valve orifice; at the same time, the liquid propellant vaporizes off.

