

EQUATION OF STATE

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Where:

n = number of moles

R = universal gas constant = 8.3145 J/mol K

N = number of molecules

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

$k = R/NA$

NA = Avogadro's number = 6.0221×10^{23}

The ideal gas law can be viewed as arising from the kinetic pressure of gas molecules colliding with the walls of a container in accordance with Newton's laws.

But there is also a statistical element in the determination of the average kinetic energy of those molecules.

The temperature is taken to be proportional to this average kinetic energy; this invokes the idea of kinetic temperature. One mole of an ideal gas at STP occupies 22.4 liters.

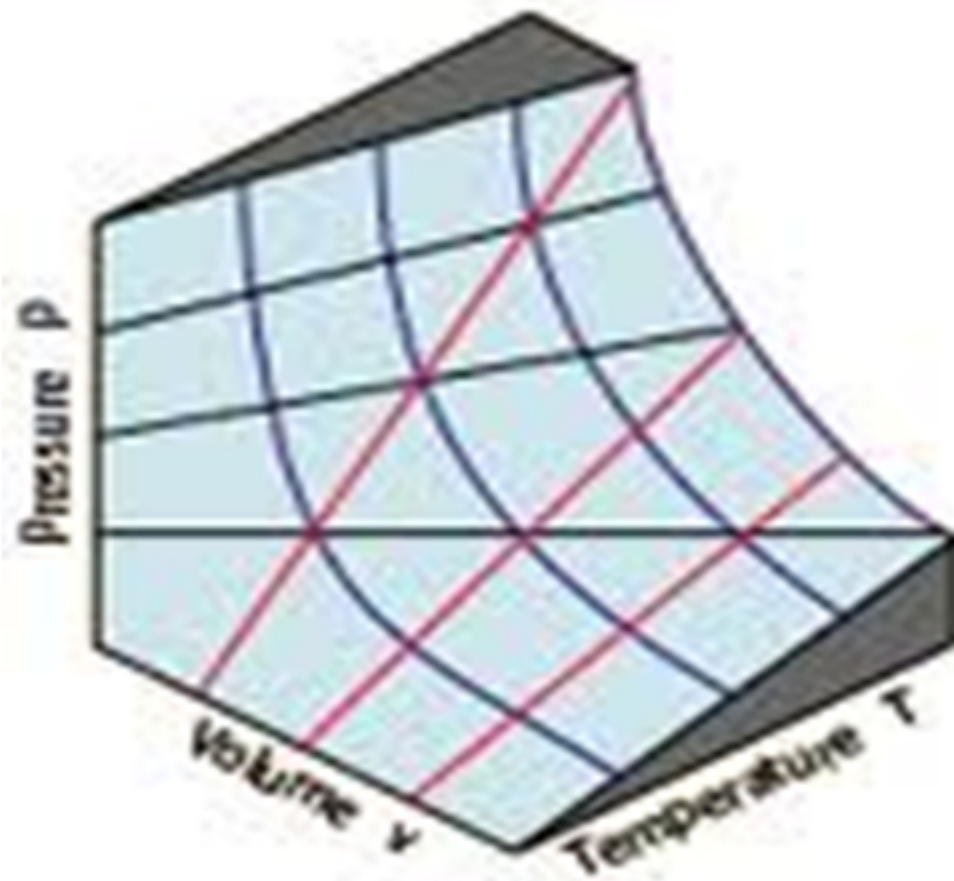
Ideal gas is a gas that have some specific criteria:

1. The number of gas particles lot but there are no attractive forces between particles
2. All particles move with a random
3. The size of the gas is very small when compared with the size of the container, so the size of the gas are ignored
4. Any collisions that occur are resilient perfect
5. Gas particles distributed evenly on the entire space in the container
6. Gas particles fulfill the law of motion newton

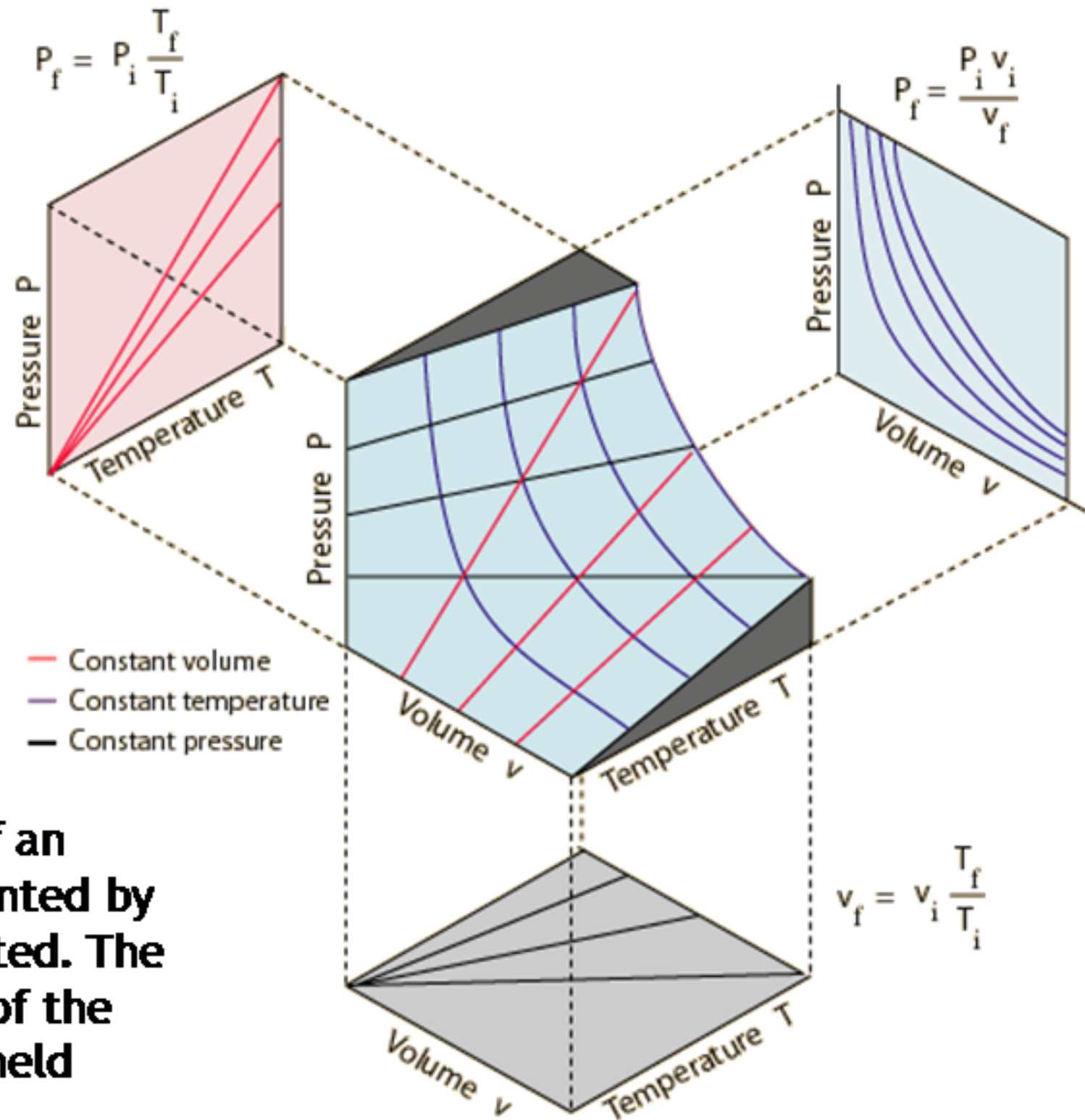
- The gas consists of objects with a defined mass and zero volume.
- The gas particles travel randomly in straight-line motion where their movement can be described by the fundamental laws of mechanics.
- All collisions involving gas particles are elastic; the kinetic energy of the system is conserved even though the kinetic energy among the particles is redistributed.
- The gas particles do not interact with each other or the with the walls of any container.
- The gas phase system will have an average kinetic energy that is proportional to temperature; the kinetic energy will be distributed among the particles according to a Boltzmann type of distribution.

P-v-T Surface for An Ideal Gas

The equation of state of a PvT system defines a surface in a rectangular coordinate system in which P , v and T are plotted along the three axes.



P-v-T surface for an ideal gas



All the possible states of an ideal gas can be represented by a PV-T surface as illustrated. The behavior when any one of the three state variables is held constant is also shown.

In an **isothermal process**, for a fixed mass of an ideal gas :

$$Pv = RT = \text{constant}$$

Robert Boyle, in 1660, discovered experimentally that *the product of the pressure and volume is very nearly constant for a fixed mass of a real gas at constant temperature.*

(Boyle's Law)

It is , exactly true for an ideal gas

BOYLE'S LAW

$$P_1 V_1 = P_2 V_2$$



In a process at **constant volume** (isochoric),
for a fixed mass of an ideal gas :

$$P = \left(\frac{nR}{V} \right) T = \text{constant} \times T$$

That is, the pressure P is a linear function of
the temperature T at constant volume.

If a process at **constant pressure** (isobaric),
for a fixed mass of an ideal gas :

$$V = \left(\frac{nR}{P} \right) T = \text{constant} \times T$$

The volume V is a linear function of the
temperature T at constant pressure

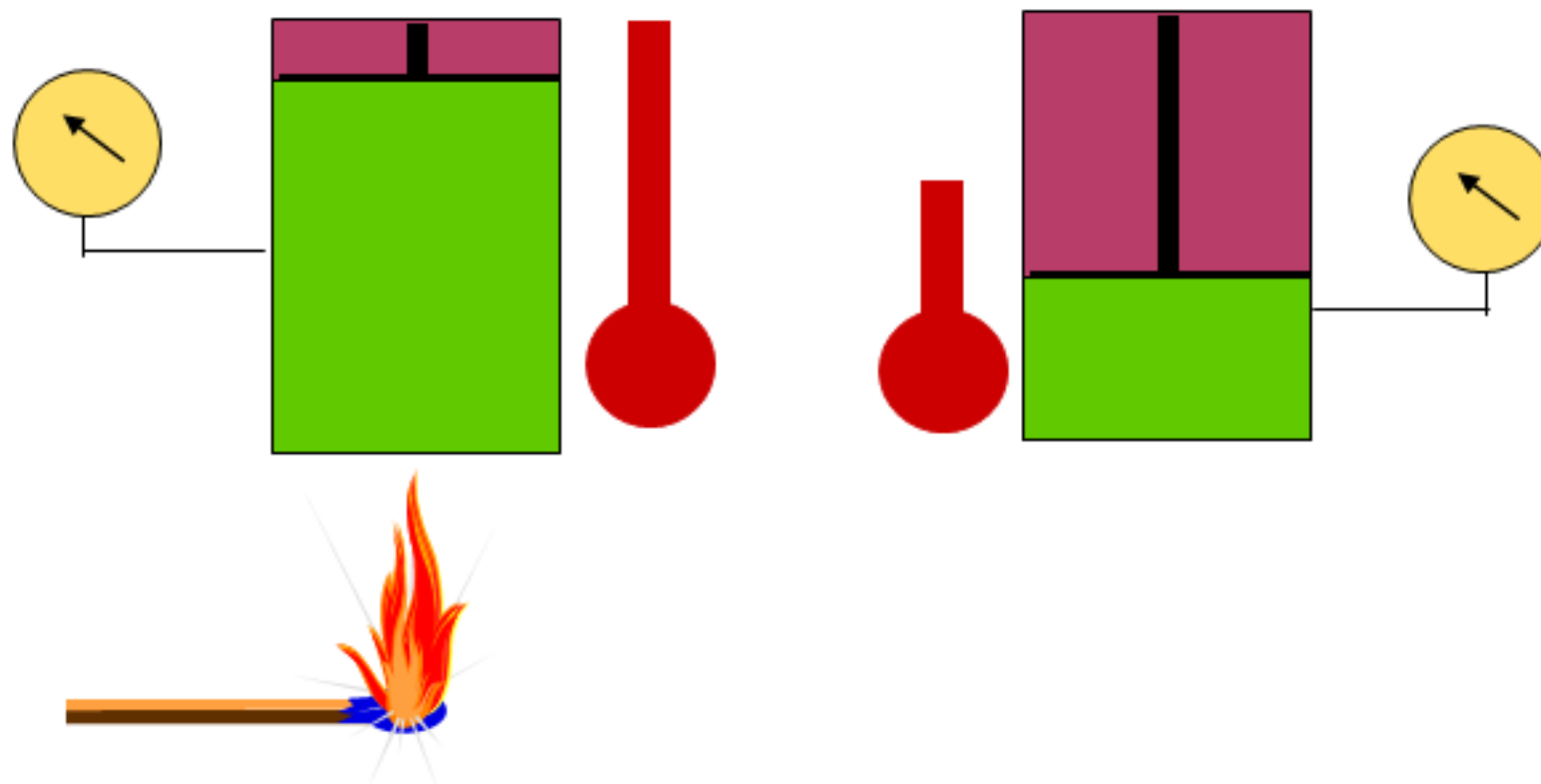
OUTLINE

- Equation of State
- Equation of State of An Ideal Gas
- P-v-T Surface for An Ideal Gas
- Equation of State of Real Gases
- P-v-T Surfaces for Real Substances
- Partial Derivative, Expansivity, and Compressibility
- Critical Constant of A Van Der Waals Gas
- Relations Between Partial Derivative

CHARLES LAW

$$V_1/V_2 = T_1/T_2$$

$$P_1V_1/T_1 = P_2V_2/T_2$$



EQUATION OF STATE OF REAL GASES

Real gases deviate from ideal gas behaviour because at low temperatures the gas molecules have less kinetic energy (move around less) so they *do* attract each other.

At high pressures the gas molecules are forced closer together so that the volume of the gas molecules becomes significant compared to the volume the gas occupies.

Under ordinary conditions, deviations from ideal gas behaviour are so slight that they can be neglected.

A gas which deviates from Ideal Gas behaviour is called a *non-ideal gas*.

The van der Waals Equation

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

Corrects for
molecular
volume

Corrects for
molecular
attraction

- General form of the van der Waals equation:

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

The term a arises from the existence of intermolecular forces.

The term b is proportional to the volume occupied by the molecules themselves.

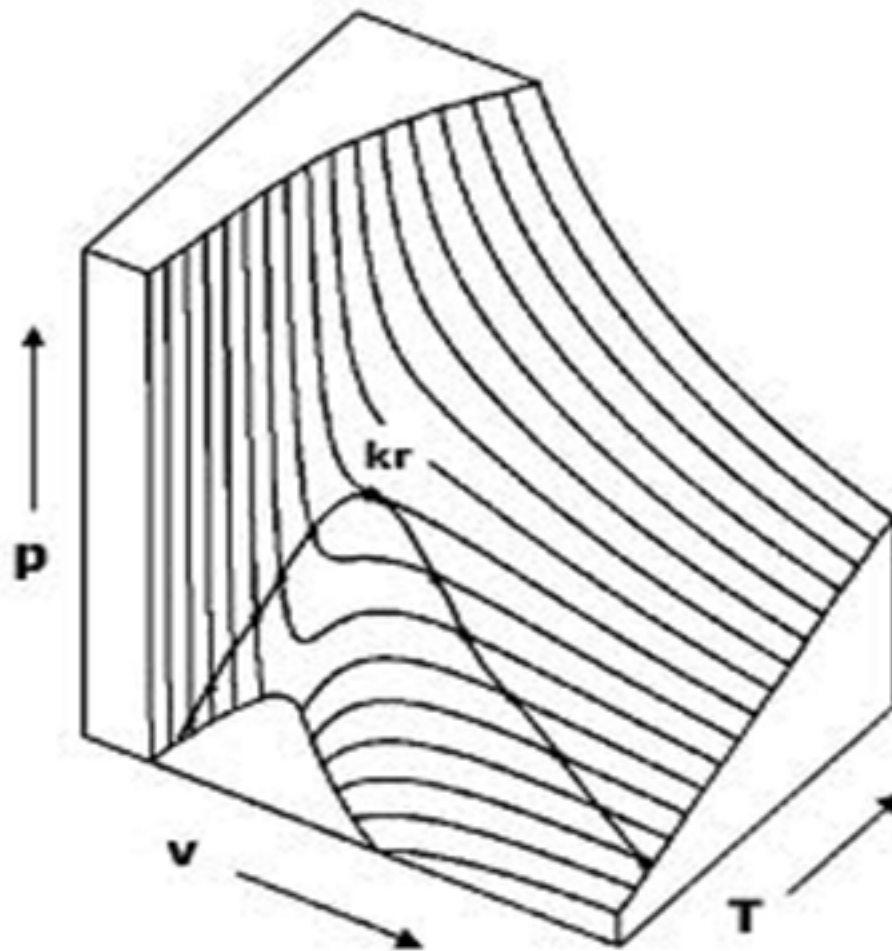
And nb is subtracted from the measured volume to represent the free volume within the gas.

Both a and b are specific values for particular gases, values that vary with temperature and pressure.

E.g. Use Van de Waal's equation to calculate the pressure exerted by 1.00 mol Cl_2 confined to a volume of 2.00 L at 273K. The value of $a=6.49\text{L}^2 \text{ atm/mol}^2$ and $b=0.0562 \text{ L/mol}$

At sufficiently large specific volumes, the term $\frac{a}{v^2}$ becomes negligible in comparison with P , and b becomes negligible in comparison with v .

The Van der Waals equation \longrightarrow
Equation of state of an ideal gas



P - v - T surface for a Van der Waals gas

Van der Waals Constants for Some Gases

Substance	a (J·m ³ /mole ²)	b (m ³ /mole)	P _c (MPa)	T _c (K)
Air	.1358	3.64x10 ⁻⁵	3.77	133 K
Carbon Dioxide (CO ₂)	.3643	4.27x10 ⁻⁵	7.39	304.2 K
Nitrogen (N ₂)	.1361	3.85x10 ⁻⁵	3.39	126.2 K
Hydrogen (H ₂)	.0247	2.65x10 ⁻⁵	1.30	33.2 K
Water (H ₂ O)	.5507	3.04x10 ⁻⁵	22.09	647.3 K
Ammonia (NH ₃)	.4233	3.73x10 ⁻⁵	11.28	406 K
Helium (He)	.00341	2.34x10 ⁻⁵	0.23	5.2 K
Freon (CCl ₂ F ₂)	1.078	9.98x10 ⁻⁵	4.12	385 K

P-V-T SURFACES FOR REAL SUBSTANCES

Simple System

A simple system is one in which the effects of motion, viscosity, capillarity, anisotropic stress, and external force fields are absent.

Homogeneous Substance

A substance that has uniform thermodynamic properties throughout is said to be homogeneous.

Pure Substance

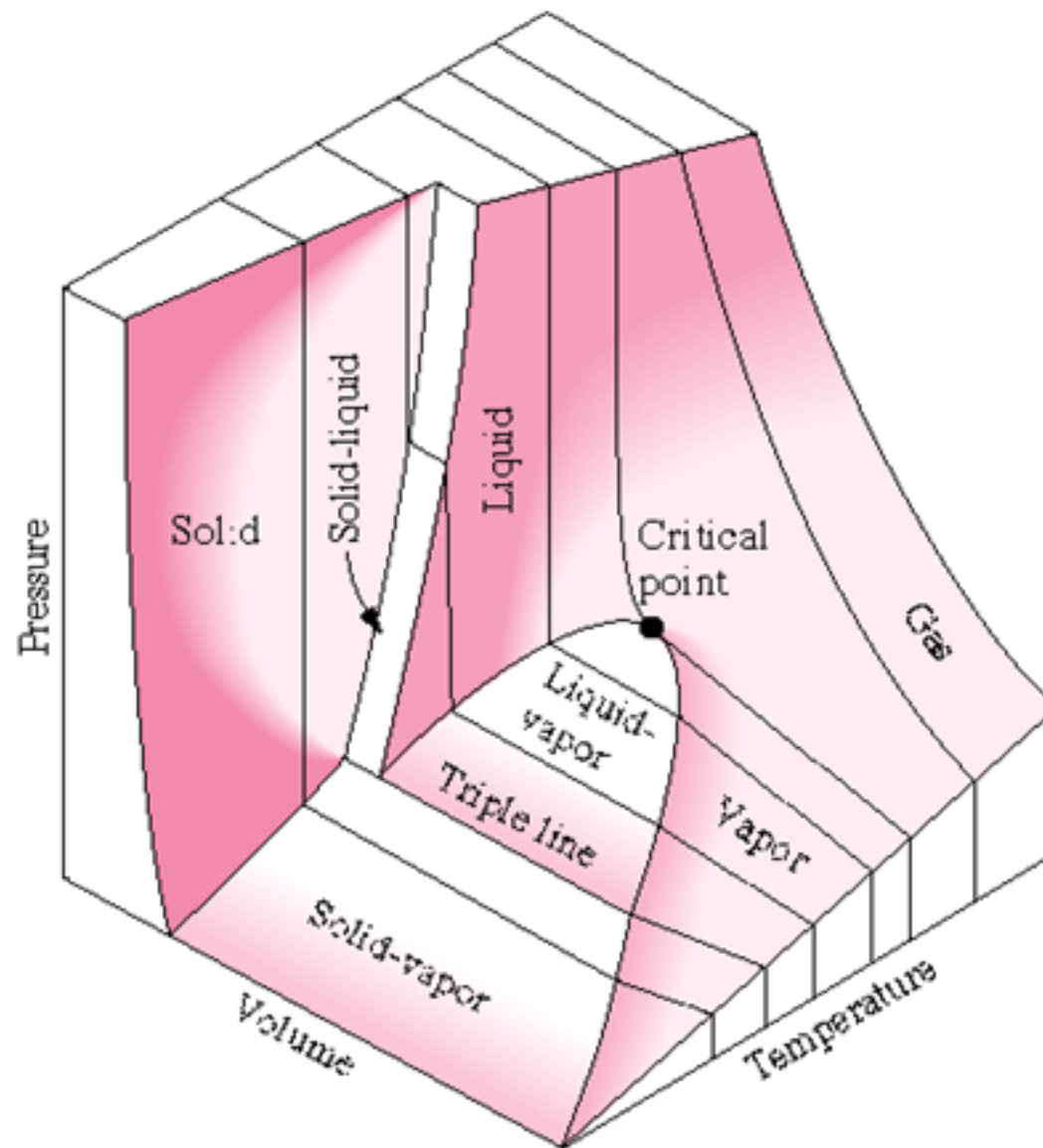
A pure substance has a homogeneous and invariable chemical composition and may exist in more than one phase.

Examples :

1. Water (solid, liquid, and vapor phases)
2. Mixture of liquid water and water vapor
3. Carbon dioxide, CO_2
4. Nitrogen, N_2
5. Mixtures of gases, such as air, as long as there is no change of phase.

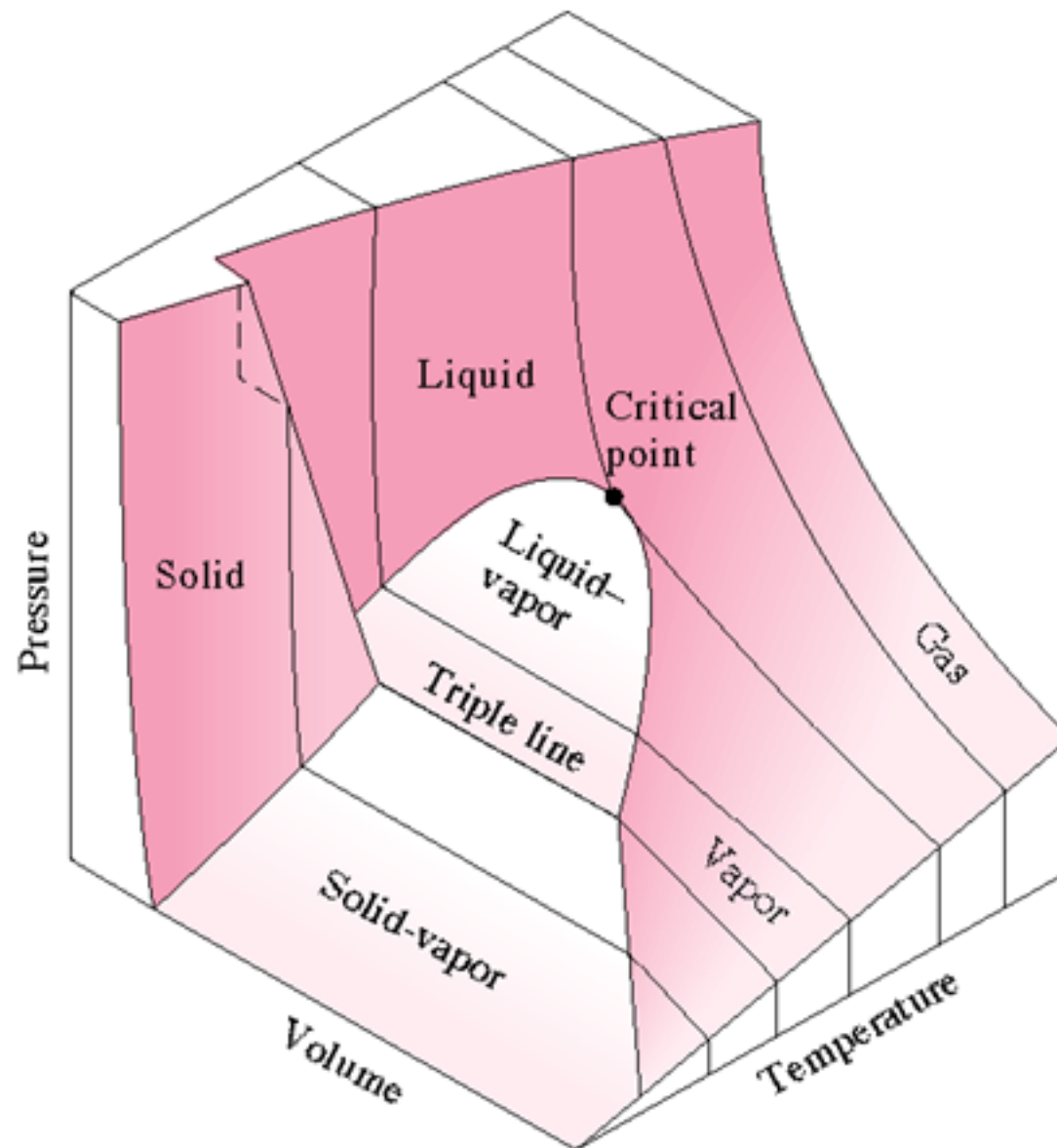
Real substances can exist in the gas phase only at sufficiently high temperatures and low pressures. At low temperatures and high pressures transitions occur to the liquid phase and the solid phase.

◆ ***P-V-T* Surface for a Substance that contracts upon freezing**



The former is for a substance like carbon dioxide

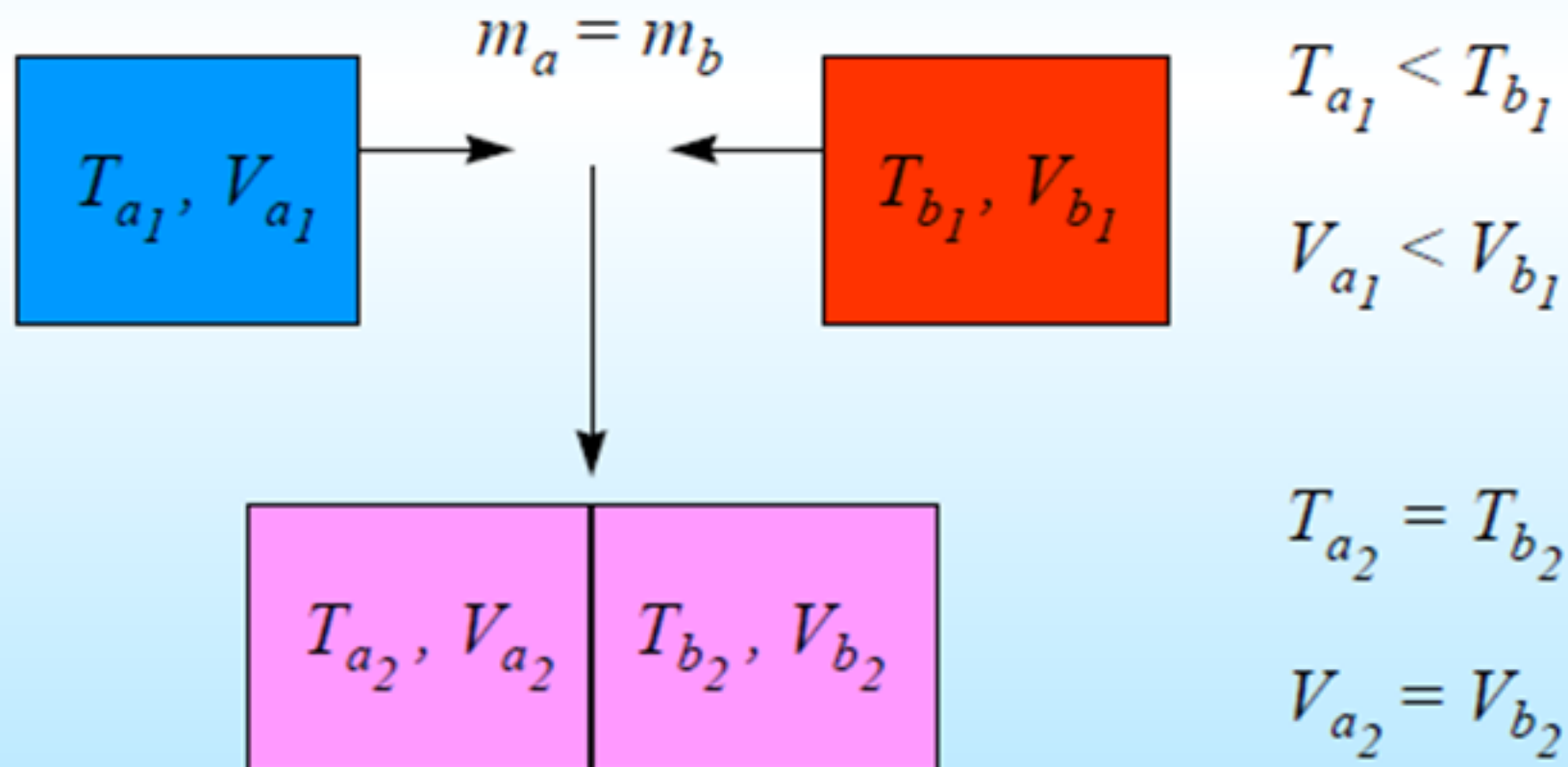
◆ ***P-V-T* Surface for a Substance that expands upon freezing**



The former is for a substance like water

Thermodynamic Process

Two copper blocks with different temperatures come into contact:



The figures shows that there are certain regions (that is, certain ranges of the variables) in which the substance can exist in a single phase only. These are the regions lettered solid, liquid and gas or vapor.

In other regions, labeled solid-liquid, solid-vapor, and liquid-vapor, two phase can exist simultaneously in equilibrium.

And along calles triple point, all three phases can coexist.

As with the P - v - T surface of an ideal gas, any line on the surface represents a possible quasisatic process, or a succession of equilibrium states.

Task

Explain the meaning of :

1. Critical point
2. Critical temperature
3. Critical pressure
4. Critical specific volume

Next meeting :

- **Partial Derivative, Expansivity, and Compressibility**
- **Critical Constant of A Van Der Waals Gas**
- **Relations Between Partial Derivative**

Thermodynamic Equilibrium

- *Thermodynamic equilibrium* is achieved when changes in thermodynamic properties cease. (i.e. pressure, volume, and temperature)
- In the example, when equilibrium is achieved there are also no further time dependent changes. Thus, the system is also at *steady state*.
- Steady state and thermodynamic equilibrium are *not* always mutual conditions.
- *Equations of state* are reserved for systems in thermodynamic equilibrium.

EQUATION OF STATE

The calculation of the properties, such as enthalpy, entropy, internal energy, etc., for different substances requires knowledge of the PVT (pressure-volume-temperature) behavior of the substance.

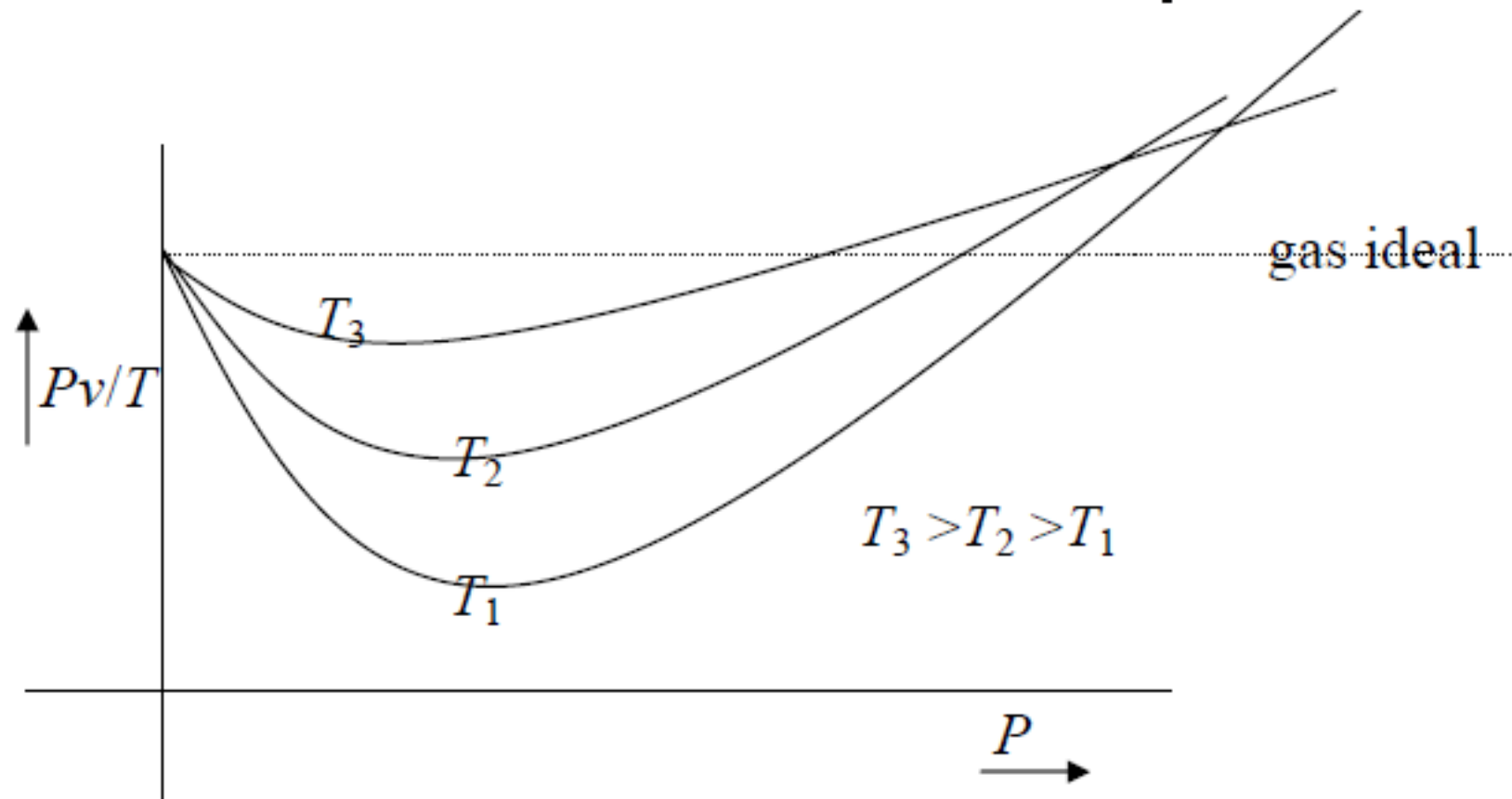
This can be given in the form of a table, graphs, or analytically.

An analytical expression to express PVT behavior is called an *equation of state*.

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

Example

Experiment for 1 mole of carbon dioxide gas.
Plot of Pv/T vs P for three different temperature :



The graph shows :

- Pv/T inconstant
- At the low temperature, all graph become one in $Pv/T = R$, with R is universal gas constant
- At the high temperature, all graph become linear

At the low sufficient pressure, all of gases :

$$Pv/T = R \text{ or } Pv = RT$$

So we often use approximation of “ideal gas” which assume that ratio of Pv/T are constant, with R for all pressure and temperature.

Naturally, there is no “ideal gas”, gas were assumed as ideal gas” at low pressure and high temperature. The study about “ideal gas” are useful for knowing the real properties of gases.

EQUATION OF STATE OF AN IDEAL GAS

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.

An ideal gas can be characterized by three state variables: absolute pressure (P), volume (V), and absolute temperature (T). The relationship between them may be deduced from kinetic theory.

It is convenient to postulate an ideal gas for which, by definition, the ratio Pv/T is exactly equal to R at all pressures and temperature

$$Pv = RT$$

or, since $v = \frac{V}{n}$

$$PV = nRT = NkT$$

Ideal gas law