# Chapter 1.  Properties of Gases

## Equation of State  (Single Component in Solid, Liqid or Gas)

The physical state of a pure substance is described by its physical properties. The state of a pure gas, for example, is specified by giving its value, $V$, $n$, $p$, and $T$.  Equation of state is an equation which interrelate these four variables:

$$p = f(T, V, n) \qquad\qquad V = f(T, p, n) \qquad\qquad \textbf{(1.A.3)}$$

**Extensive Properties**: properties proportional to the amount of material.

e.g., **mass, volume, number of moles, heat capacity**.

**Intensive Properties**: the nature of materials not depending upon the amount.

e.g., **temperature, pressure, diffusivity, viscosity,**

**thermal conductivity, dielectric constant,**

**electrical conductivity, electronic conductivity, ionic conductivity,**

**heat capacity / mole,    heat capacity / atom, etc.**

For a homogeneous material, only two intensive variables can be independent; the remaining variables must then be a function of these two.

**Intensive Property:** $f(P,T)$ **or** $f(\sigma,P)$
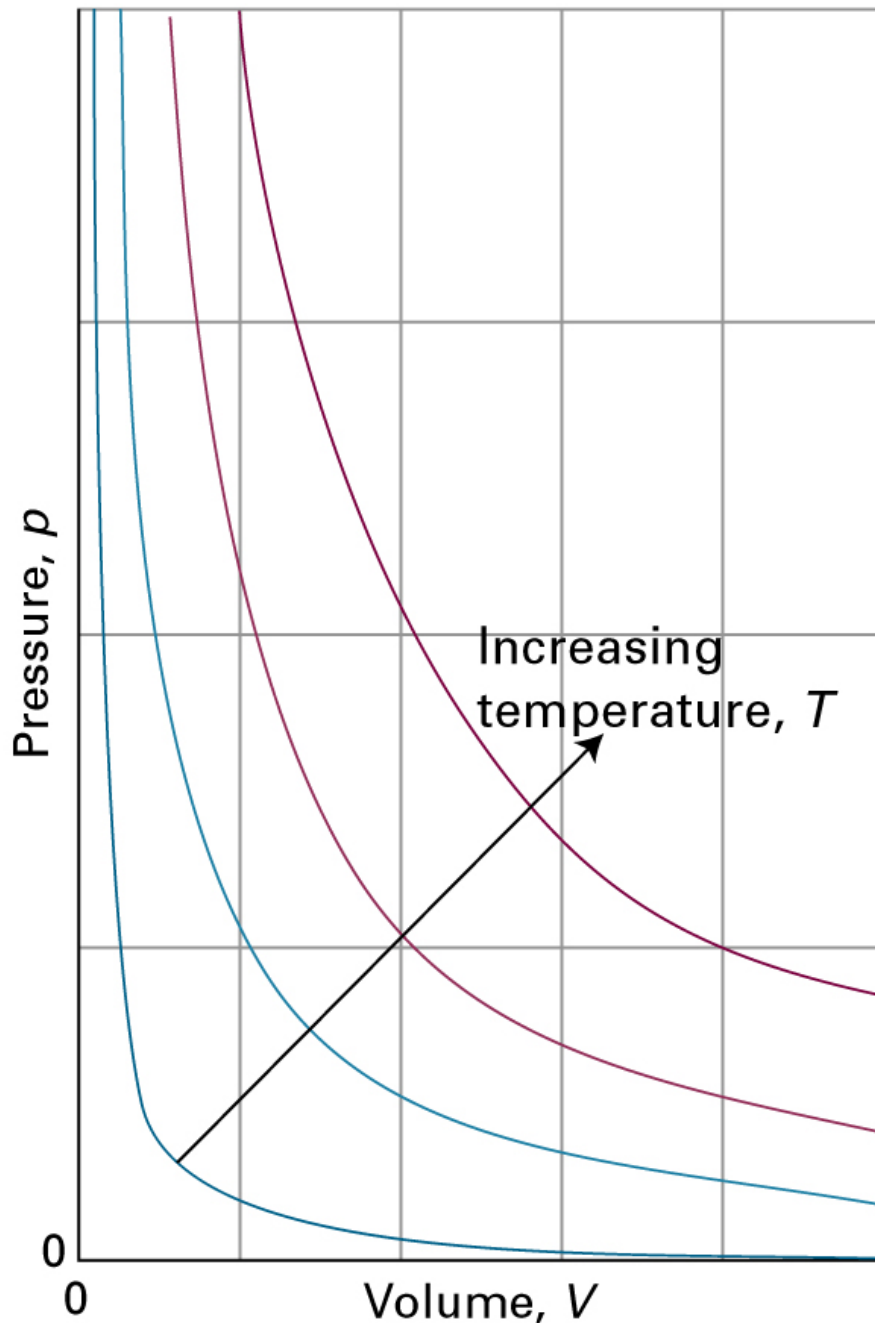
Equation of state ⟷ Functional dependence of any other physical properties on these two variables.

**Single Component in Solid, Liqid or Gas**

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## 1.A.2. The Ideal Gas Law (Perfect Gas) Single Component

Ideal Gas: **1. The size of molecule is negligibly small.**

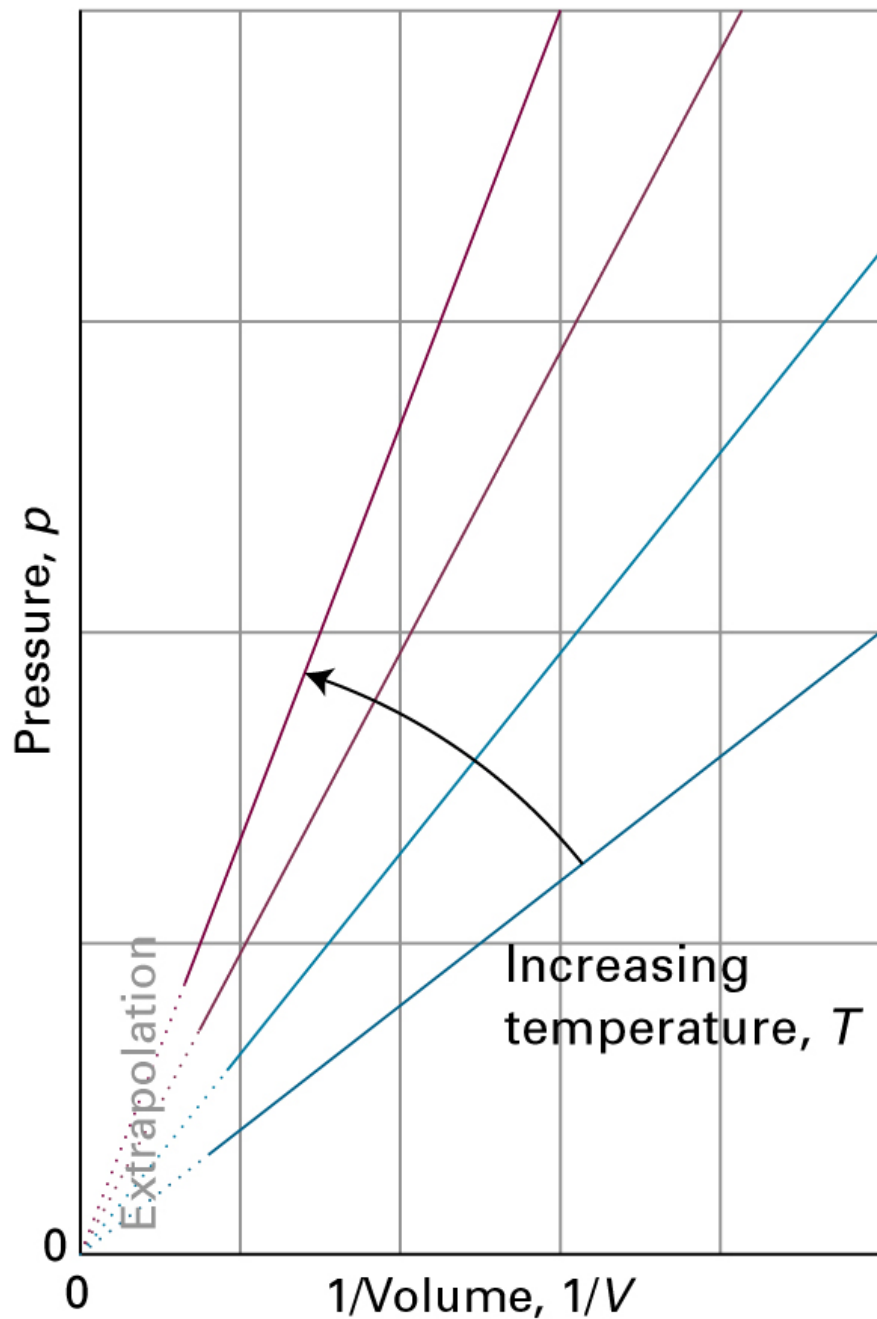**2. The interactions between molecules do not exist.**

$$p\,V = n\,R\,T \qquad p\,V = N\,k_B\,T$$

$$p\,V = N\,k_B\,T$$

**Figure 1.A.2**
The pressure-volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV$ = constant) and is called an isotherm.

The graph axes are labeled "Pressure, $p$" (vertical) and "Volume, $V$" (horizontal), with an arrow indicating "Increasing temperature, $T$".

Pressure, $p$

Extrapolation

Increasing temperature, $T$

0

0    1/Volume, 1/$V$

$$p = N\,k_B\,T\,/\,V$$

**Figure 1.A.3**
Straight lines are obtained when the pressure is plotted against 1/$V$.

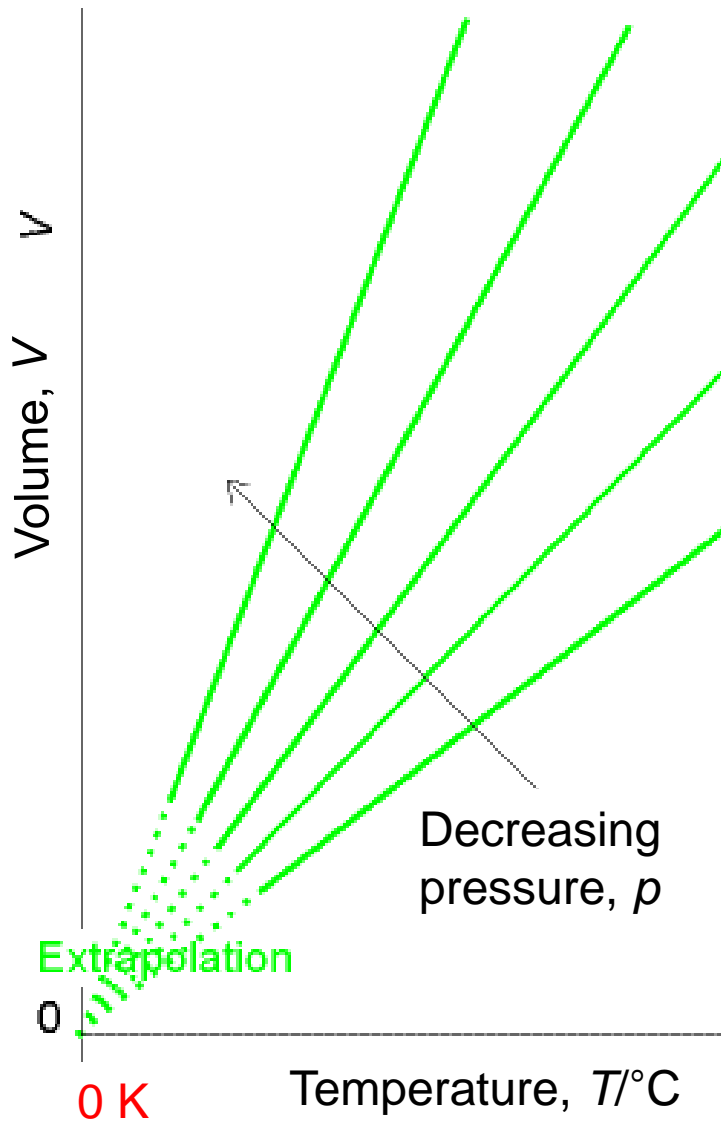$$V = N\,k_B\,T\,/\,p$$

**Figure 1.A.4**
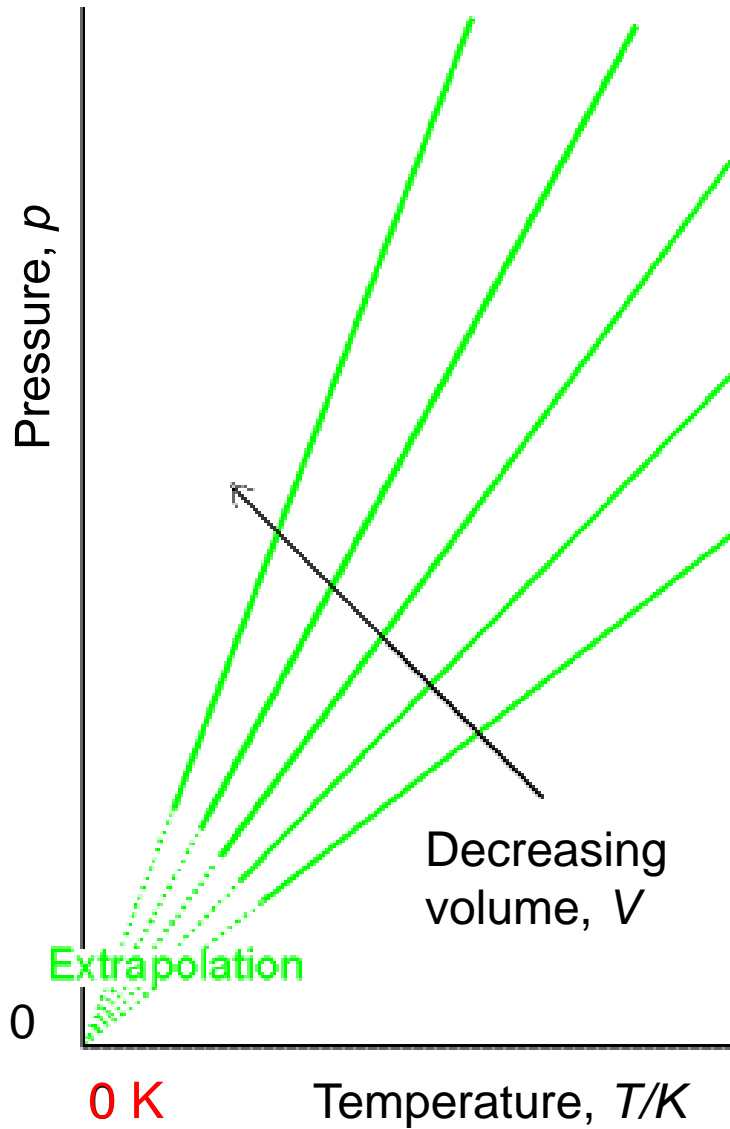The variation of volume of a fixed amount of gas with the temperature at **constant pressure (isobar).**
Note that in each case they extrapolate to zero volume at -273.15°C.

*by Experimentalists*

**(at the given pressure)**

Volume, $V$

$V$

Extrapolation

0

0 K

Decreasing pressure, $p$

Temperature, $T$/°C

"I take my blood pressure medicine at bedtime and before looking at the market reports."

**Pressure, p** *(vertical axis)*

**Temperature, T/K** *(horizontal axis)*

0 K

0
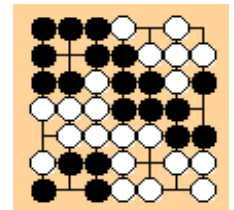
Extrapolation

Decreasing volume, V

$$p = N\,k_B\,T\,/\,V$$

**Figure 1.A.5**
The pressure also varies linearly with the temperature at **constant volume**, and extrapolates to zero at $T = 0$ K ($= -273.15°$C).
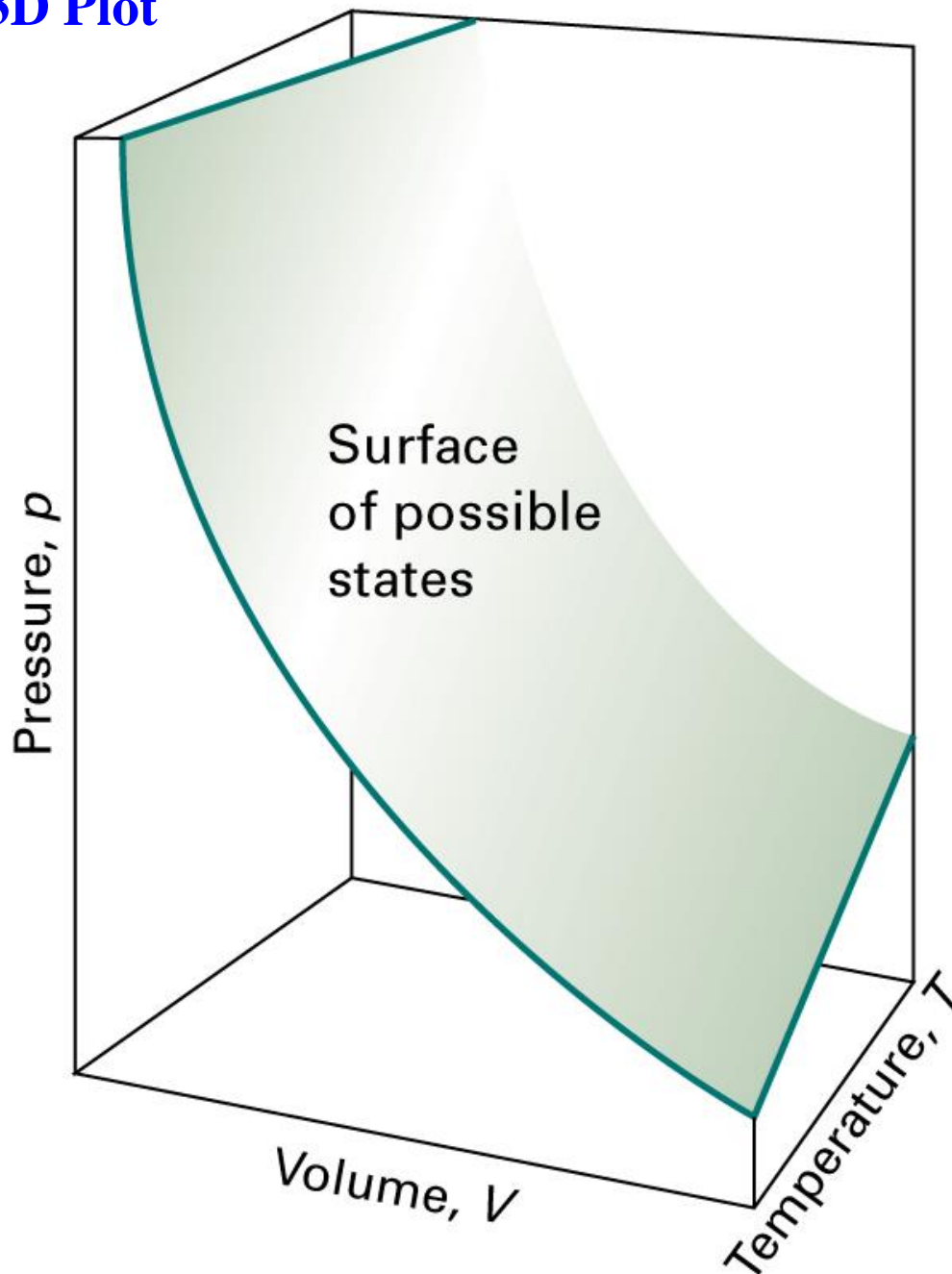
*by Theoreticians*

**(at the given volume)**

~2 Å
Lattice Constant

Surface
of possible
states

Pressure, $p$

Volume, $V$
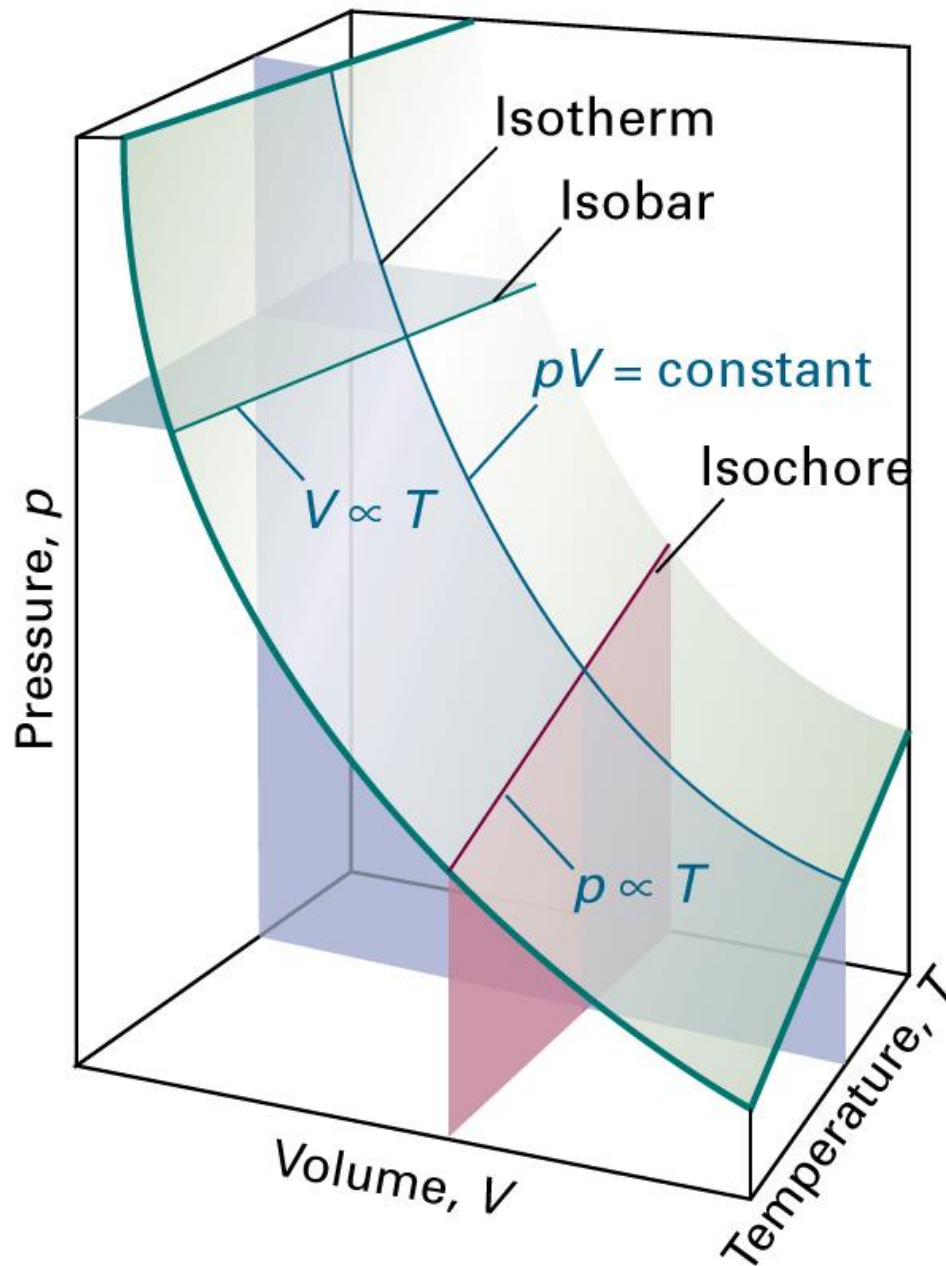
Temperature, $T$

$$p\,V = N\,k_B\,T$$

**Figure 1.A.6**
A region of the $p$, $V$, $T$ surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

$$p\,V = N\,k_B\,T$$

**Figure 1.A.7**

Sections through the surface shown at a constant variable.

# 1.B. The Kinetic Model of Gases

Three Assumptions:

1. The gas consists of molecules of mass *m* in **ceaseless (elastic) random motion**.

2. The **size** of molecules is **negligible**, in the sense that their diameters are much smaller than the average distance traveled between collisions.

3. The molecules **do not interact,** except that they make perfectly **elastic collisions** when they are in contact.

   An elastic collision means that the

   **total translational kinetic energy** of a colliding pair is

   the same before and after the collision:

   *no* energy is left in one of the colliding particles

   as *rotational energy* or *vibrational energy*, etc.

The **collision frequency**, $z$ = the number of collisions made by a single particle per time
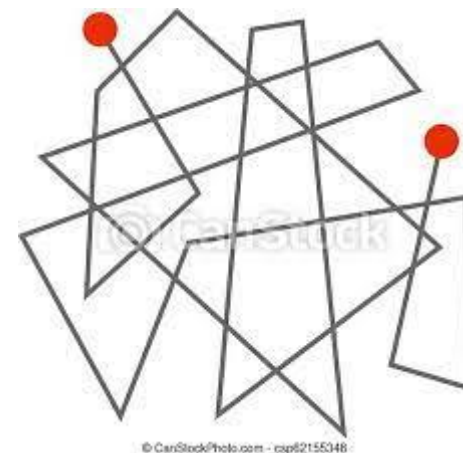
$$z^{-1} = \tau : \textbf{Collision Time}$$

The **mean free path**, $\lambda$ = the average distance each particle travels between collisions

$$\sigma = ne^2 \tau / m^*$$

*free electron model
in solid*

## 1.B.1(a). The Pressure Exerted by a Gas

When a molecule of mass $m$ collides with the wall perpendicular to the $x$-axis, its component of momentum along the $x$-axis changes from $mv_x$ to $-mv_x$. The total change of momentum on each collision is of magnitude $|2mv_x|$.
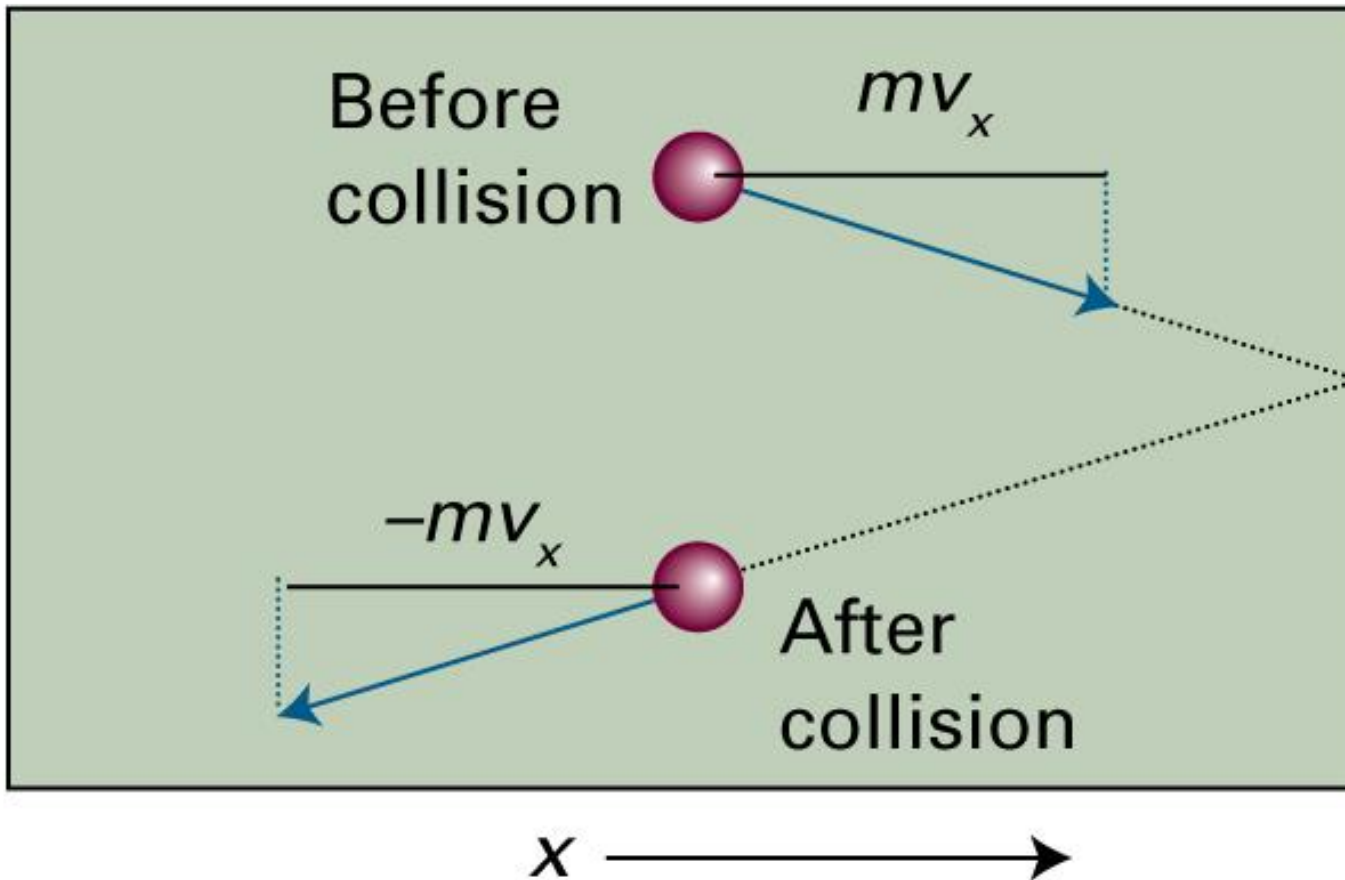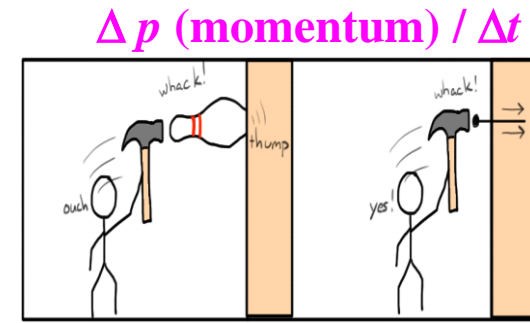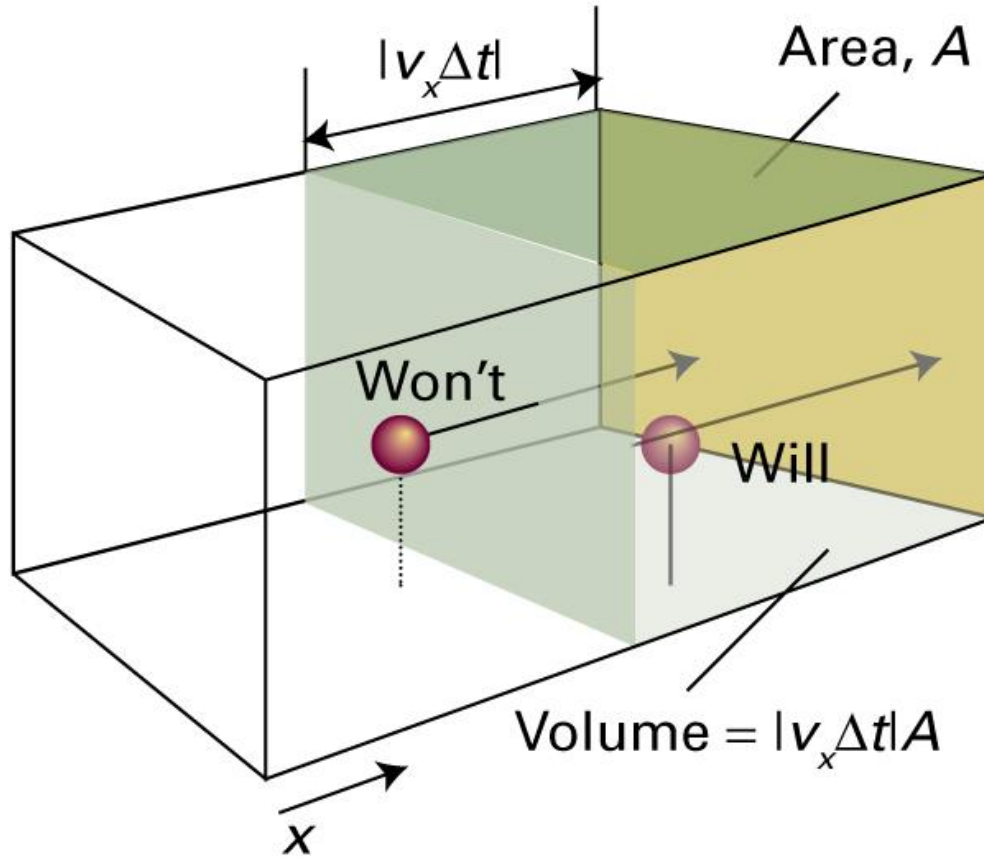
**Figure 1.B.1**
The pressure of a gas arises from the impact of its molecules on the walls.
In **an elastic collision** of a molecule with a wall perpendicular to the $x$-axis,
the $x$-component of velocity is reversed, but the $y$- and $z$-components are
unchanged.

The number of collisions in a time interval **Δ*t***

$\cong$

The number of molecules able to reach in that time

$|v_x \Delta t|$

Area, A

Won't

Will

Volume $= |v_x \Delta t| A$

x

**Figure 1.B.2**
A molecule will reach the wall on the right within an interval $\Delta t$
if it is within a distance $v_x \Delta t$ of the wall and traveling to the right.

The distance **<u>a molecule of velocity $v_x$</u>** can travel in a time $\Delta x = |v_x| \Delta t,$ so all the molecules lying within a distance $|v_x| \Delta t$ of the wall will strike it if they are traveling towards it.

$A$ : the cross-section of the container

$\dfrac{nN_A}{V}$ : the <u>number of molecules per volume</u>

All the molecules lying in a volume $A|v_x| \Delta t$ will reach the wall.

$\therefore \dfrac{nN_A \; A|v_x| \Delta t}{V}$ : the number of molecules <u>in the volume of interest</u>

On the average, half of these are moving to the right, and half to the left, and so <u>the average number of collisions in the interval $\Delta t$</u> is $\dfrac{nN_A \; A|v_x| \Delta t}{2V}$

$\therefore$ the total <u>momentum change</u>

$$= \frac{nN_A \; Av_x \Delta t}{2V} \times 2mv_x = \frac{nmN_A \; Av_x^2 \Delta t}{V} = \frac{nMAv_x^2 \Delta t}{V} \qquad \text{where } M = mN_A$$

The rate of change of momentum = **<u>force</u>** $= \dfrac{nMAv_x^2}{V}$

The pressure $= \dfrac{nMv_x^2}{V}$

Not all the molecules travel with the same velocity, and so the detected pressure is the average quantity just calculated.

$$p = \frac{nM \langle v_x{}^2 \rangle}{V}$$

Since the motion of the molecules is random,

$$\langle v_x{}^2 \rangle = \langle v_y{}^2 \rangle = \langle v_z{}^2 \rangle$$

$$v^2 = v_x{}^2 + v_y{}^2 + v_z{}^2$$

$$\langle v^2 \rangle = \langle v_x{}^2 \rangle + \langle v_y{}^2 \rangle + \langle v_z{}^2 \rangle = 3 \langle v_x{}^2 \rangle, \qquad \langle v_x{}^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$\langle v^2 \rangle$ :  mean square speed of the molecules   **→ mean energy**

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$ **root mean square (rms) speed**

$$\therefore p = \frac{nM \langle v_x{}^2 \rangle}{V} = \frac{nM \langle v^2 \rangle}{3V}$$

$$\therefore pV = \frac{1}{3} nM (v_{rms})^2 = \frac{1}{3} Nm (v_{rms})^2$$

$$pV = \frac{1}{3}nM(v_{rms})^2 = nRT = Nk_BT$$

$$\frac{3}{2}k_BT = \frac{1}{2}m\langle v^2 \rangle$$

$$v_{rms} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

**root mean square speed of molecules**

## 1.B.1(b). Maxwell-Boltzmann Distribution of Molecular Speeds

In an actual gas, the speeds of individual molecules span a wide range, and the collisions in the gas **continually redistribute** the speeds among the molecules.

The probability that a molecule has a velocity with components in the range $v_x$ to $v_x + dv_x$, $v_y$ to $v_y + dv_y$, and $v_z + dv_z = f(v_x, v_y, v_z)dv_x dv_y dv_z$.

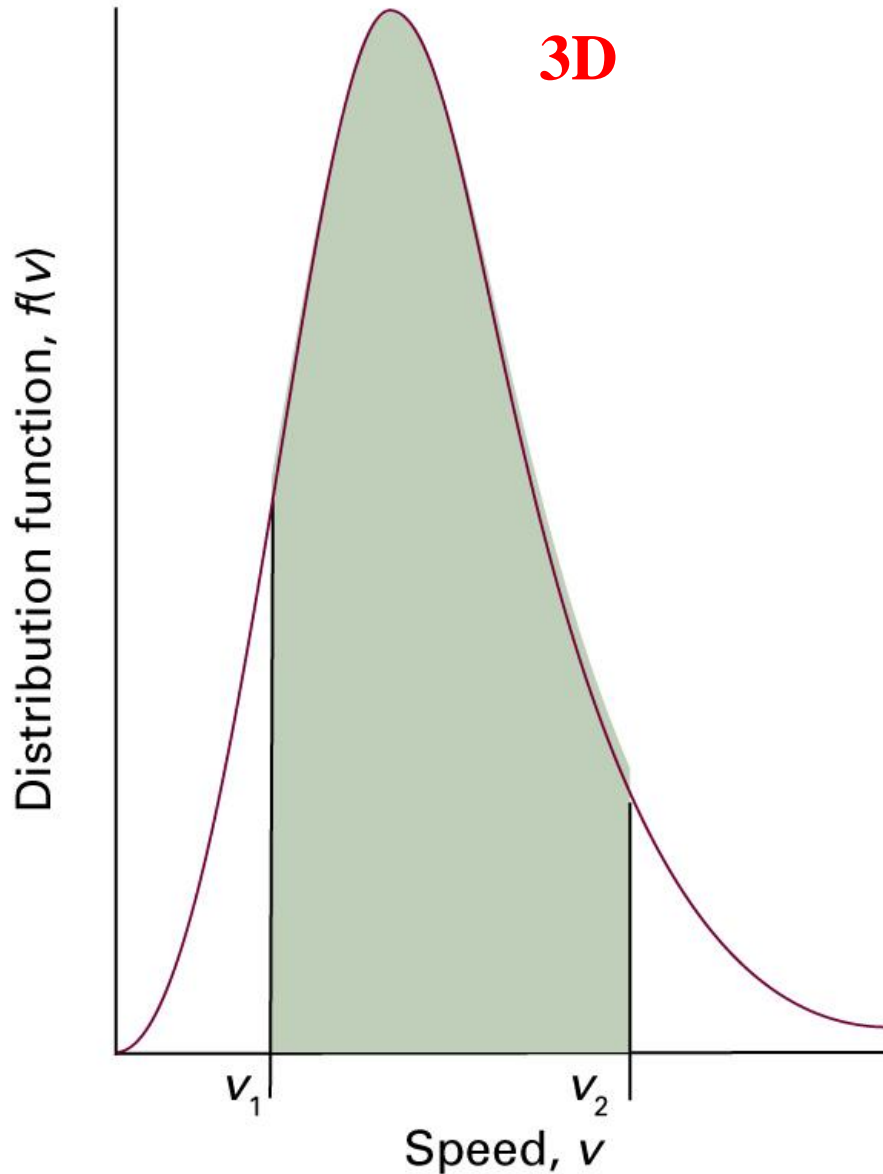Fraction in the range $v_1$ to $v_2 = \int_{v_1}^{v_2} f(v)dv$

**3D**

**Figure 1.B.6**
To calculate the probability that a molecule will have a speed **in the range $v_1$ to $v_2$**, we integrate the distribution between those two limits.

**3-D**

$$V_{rms} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

Distribution function, $f(v)$

Low temperature
or
high molecular mass

Intermediate
temperature or
molecular mass

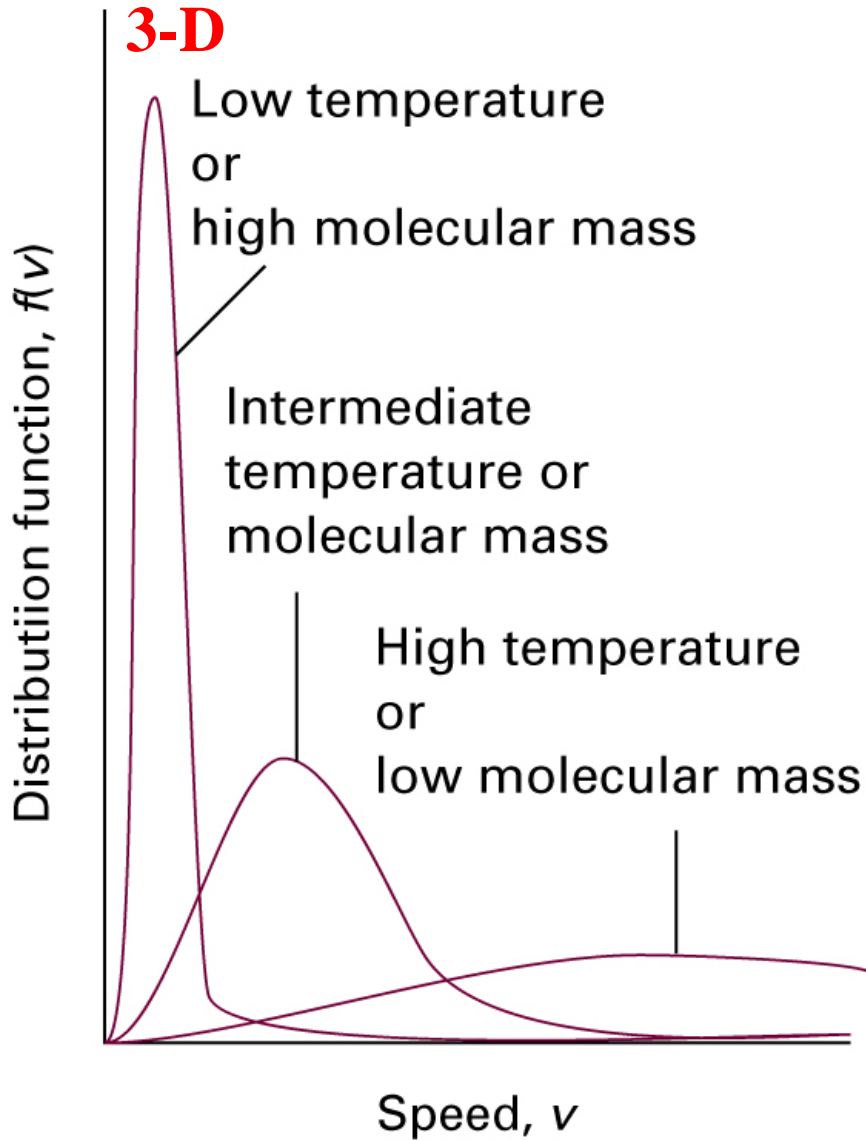High temperature
or
low molecular mass

Speed, $v$

**Figure 1.B.4**
The distribution of molecular speeds with temperature or molar mass.

Note that the most probable speed (corresponding to the peak of the distribution) **increases with temperature and with decreasing mass**, and simultaneously, the distribution becomes broader.

The distribution $f(v_x, v_y, v_z)$ can depend only on the speed $v$, where

$$v^2 = v_x{}^2 + v_y{}^2 + v_z{}^2,$$

The evaluation of $K$

**Why $\delta v_x$ , not $\delta E$ ?**

$$\int_{-\infty}^{\infty} f(v_x)\, dv_x = 1$$

$$\int_{-\infty}^{\infty} f(v_x)\, dv_x = K \int_{-\infty}^{\infty} e^{-\frac{mv_x{}^2}{2kT}} dv_x = K\left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}} = 1$$

**Boltzmann Distribution
(Derivation in Sec. 15A.2)**

$$\therefore K = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \qquad (v_x)_{rms} = \left(\frac{kT}{m}\right)^{\frac{1}{2}}$$

**1D**

$$\therefore f(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x{}^2}{2kT}}$$

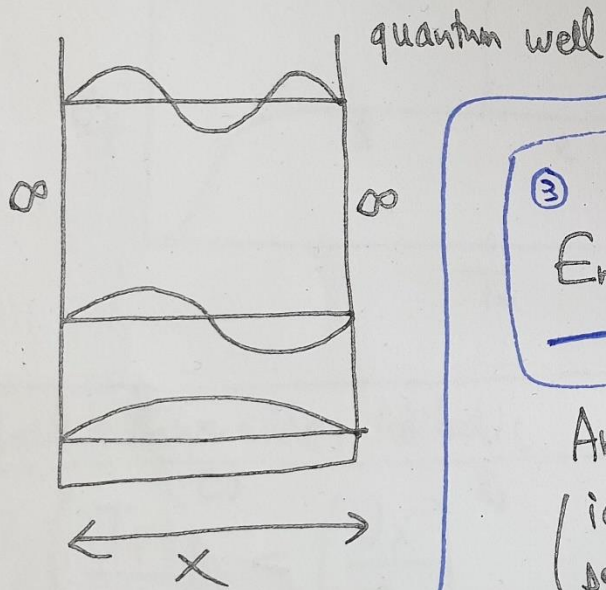**Maxwell-Boltzmann distribution of molecular velocities**

**(1.B.5)**

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

For three-dimensional case, the Maxwell-Boltzmann distribution:

$$f(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = f(v_x) f(v_y) f(v_z)\, dv_x\, dv_y\, dv_z$$

**3D**

$$= \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} dv_x\, dv_y\, dv_z$$

# Particle in a Box

quantum well

$$P = \frac{h}{\lambda} = \hbar k \quad (k = \frac{2\pi}{\lambda})$$
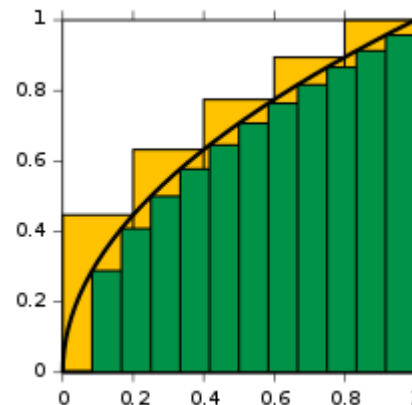
③ $$E_n = \frac{h^2 \, n^2}{8m \, X^2} \qquad n = 1, 2, 3, \ldots$$

② $$\vec{P} = \frac{h \cdot n}{2X} = m\vec{v}$$

① $$\lambda = \frac{2X}{n}$$

Ar gas    $X = 10$ cm

(ideal gas)
(perfect gas)   size zero
                intention zero



Approximations to integral of $\sqrt{x}$ from 0 to 1, with 5 yellow right endpoint partitions, and with 12 green left endpoint partitions.
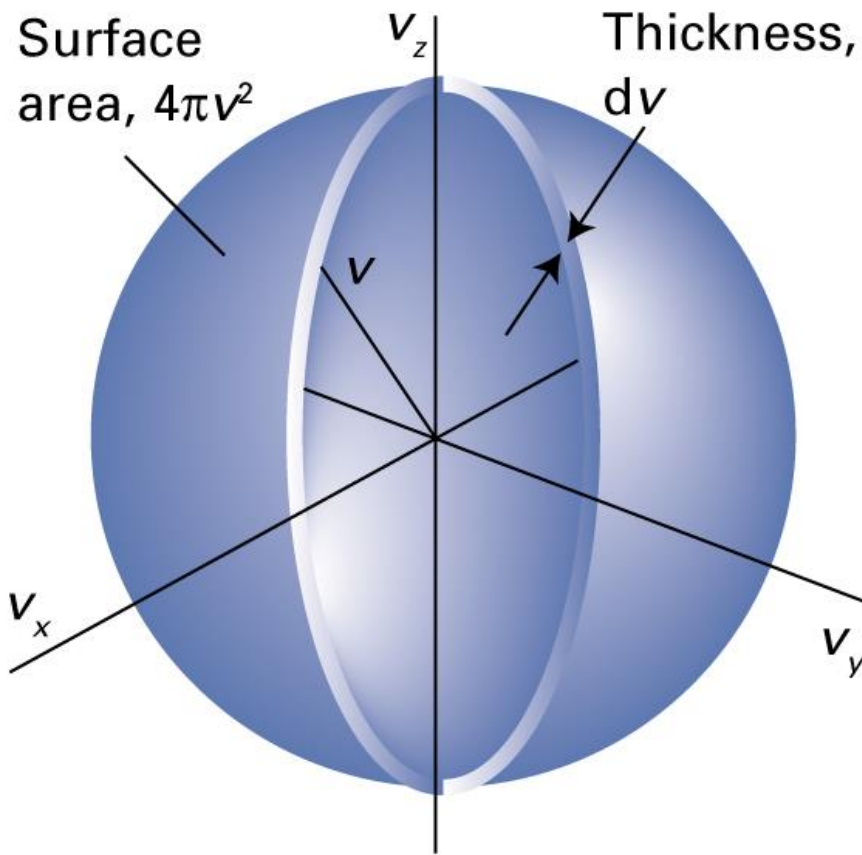
**Surface area, $4\pi v^2$**

**Thickness, $dv$**

The volume of spherical shell $= 4\pi v^2 dv$

The probability that the speed lies in the range $v$ to $v+dv$ irrespective of direction of motion:

$$f(v)dv = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} \, 4\pi v^2 dv$$

$$\therefore f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$$

**3D**

**Figure 1.B.3**
The probability $f(v)dv$ that the molecule has a speed in the range $v\left(=\sqrt{v_x^2+v_y^2+v_z^2}\right)$ to $v+dv$ is the sum of the probabilities that it lies in any way of the volume elements $dv_x dv_y dv_z$ in a spherical shell of radius $v$.

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}$$

**1D**  $\approx$ **Boltzmann Distribution**

(1)  The <u>root mean square speed</u> is the square root of the average value of $v^2$.

*now proved*

$$v_{rms} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

**ppt 0-11**
**ppt 1-15**

**(1.B.7)**

(2)  The <u>mean speed</u> is the mean of the speeds calculated using the Maxwell-Boltzmann distribution.

$$\langle v \rangle = \int_0^\infty v f(v)\, dv = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

**(1.B.7)**

(3) The <u>most probable speed</u> is the speed at which the Maxwell-Boltzmann distribution passes through a maximum.

$$v_{most\ probable} = \left(\frac{2RT}{M}\right)^{\frac{1}{2}}$$

**(1.B.9)**

(4) The **relative mean speed**  $v_{rel} = \sqrt{2}\, v_{mean} = \sqrt{2}\langle v \rangle$

For two dissimilar molecules of masses $m_A$ and $m_B$,

$$v_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}, \text{ where } \mu = \frac{m_A m_B}{m_A + m_B}$$

**(1.B.10a)**

$$c^* = (2RT/M)^{1/2}$$

$$\bar{c} = (8RT/\pi M)^{1/2}$$

$$c = (3RT/M)^{1/2} = v_{rms} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$
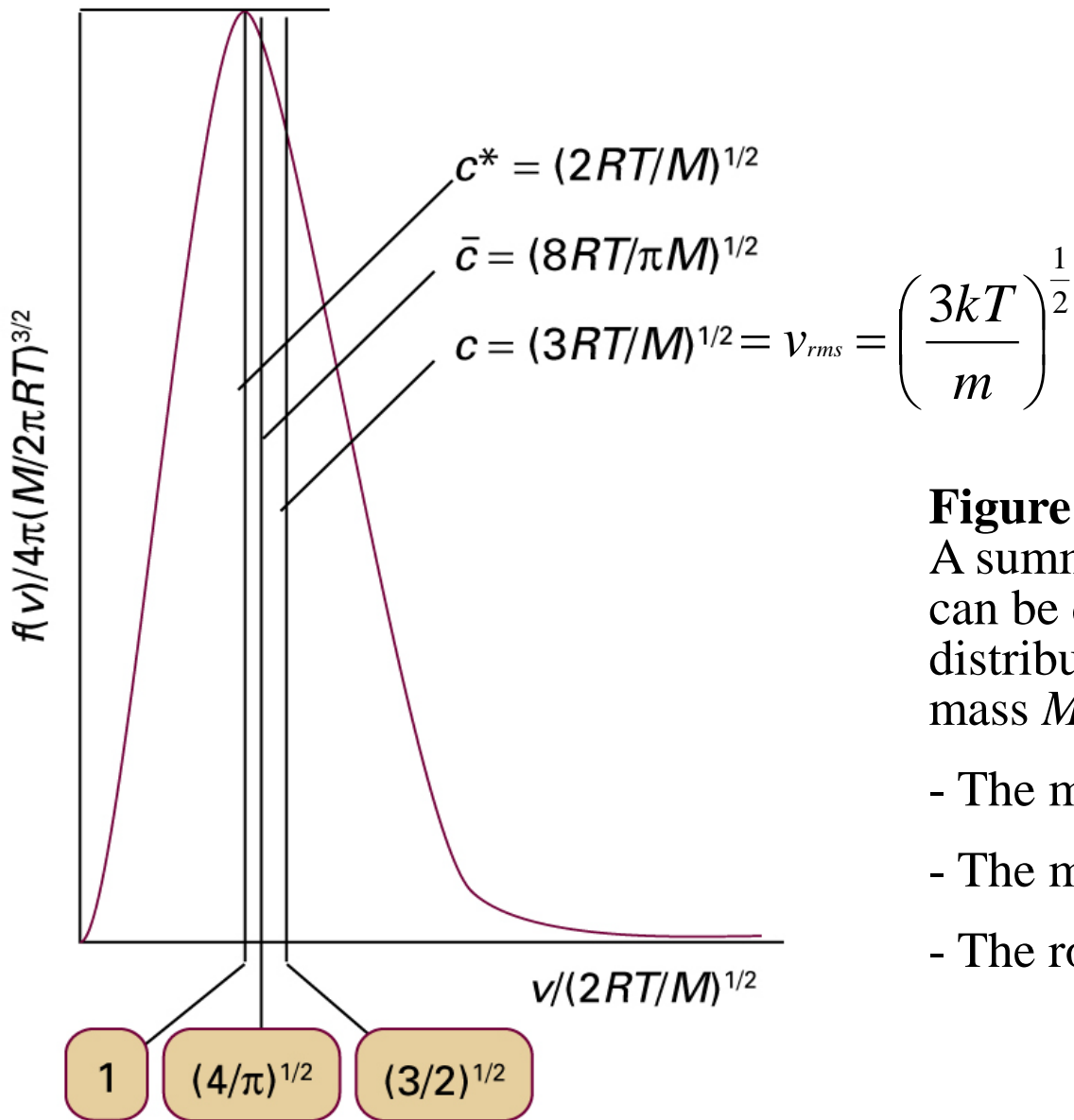
**Figure 1.B.7**
A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass $M$ at a temperature $T$:

- The most probable speed.

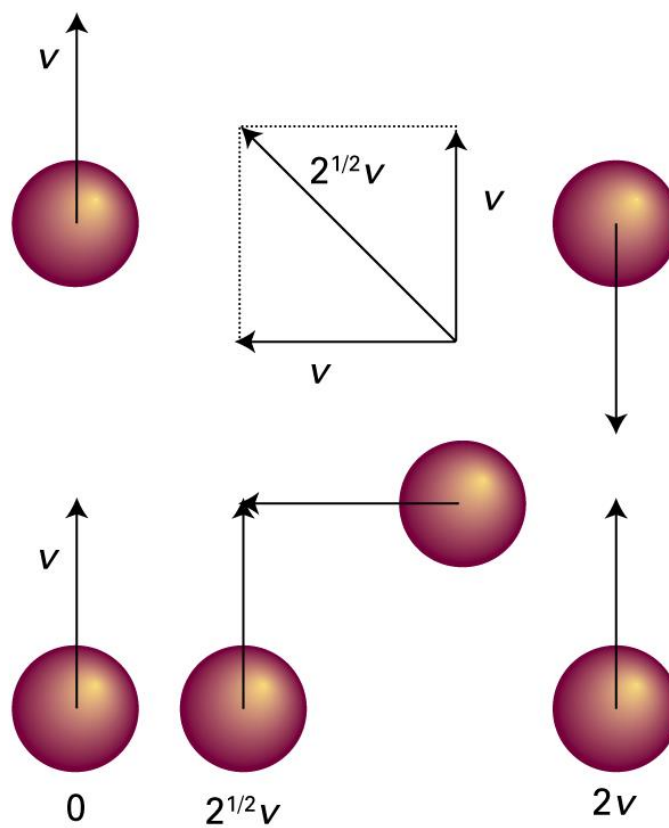- The mean speed.

- The root mean square speed.

**Figure 1.B.8**

A simplified version of the argument to show that the **mean relative speed** of molecules in a gas is related to the mean speed.

When the molecules are moving in the same direction, the mean relative speed is **zero**.

It is **2v** when the molecules are approaching each other.

The mean relative speed is $\sqrt{2}v$   (as confirmed by more detailed calculation).

# Neutral Molecule
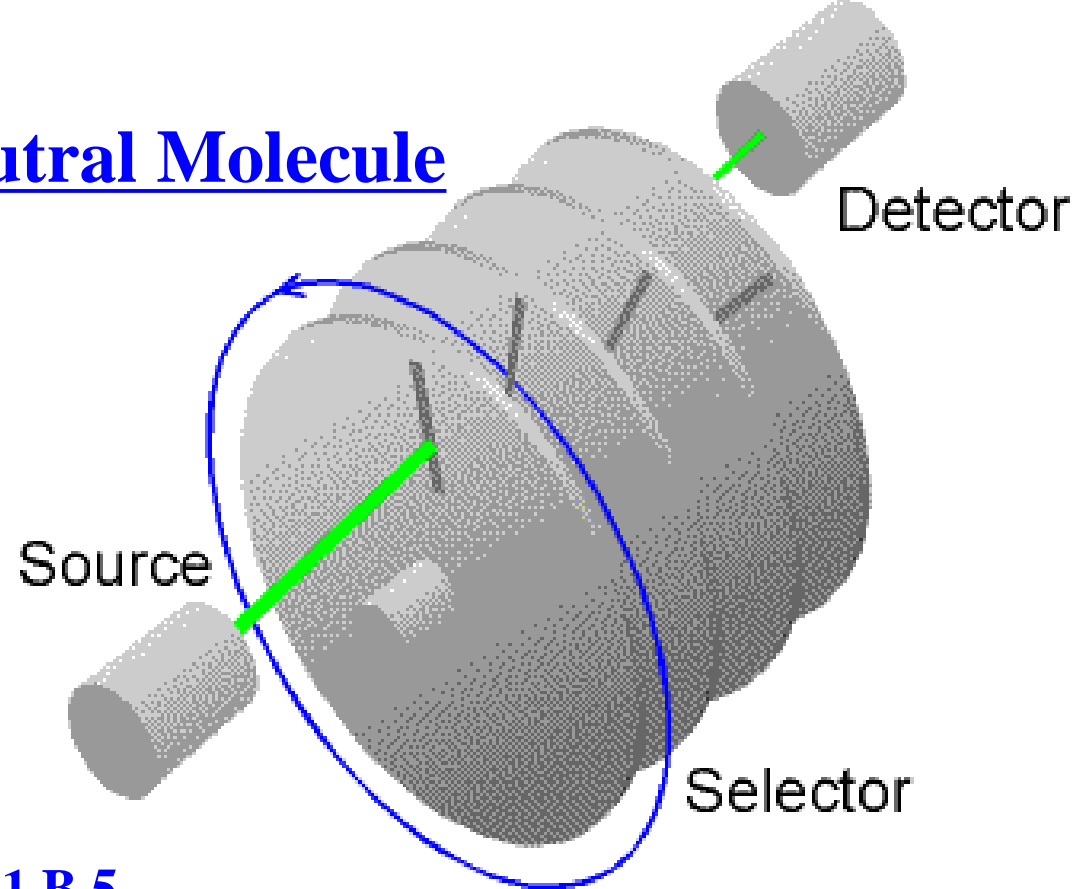
## Charged Molecule
**charge/mass (= $q/m$)**
**through $B$**
**(magnetic field)**

### ToF-SIMS

**(Secondary Ion Mass Spectroscopy)**

Detector

Source
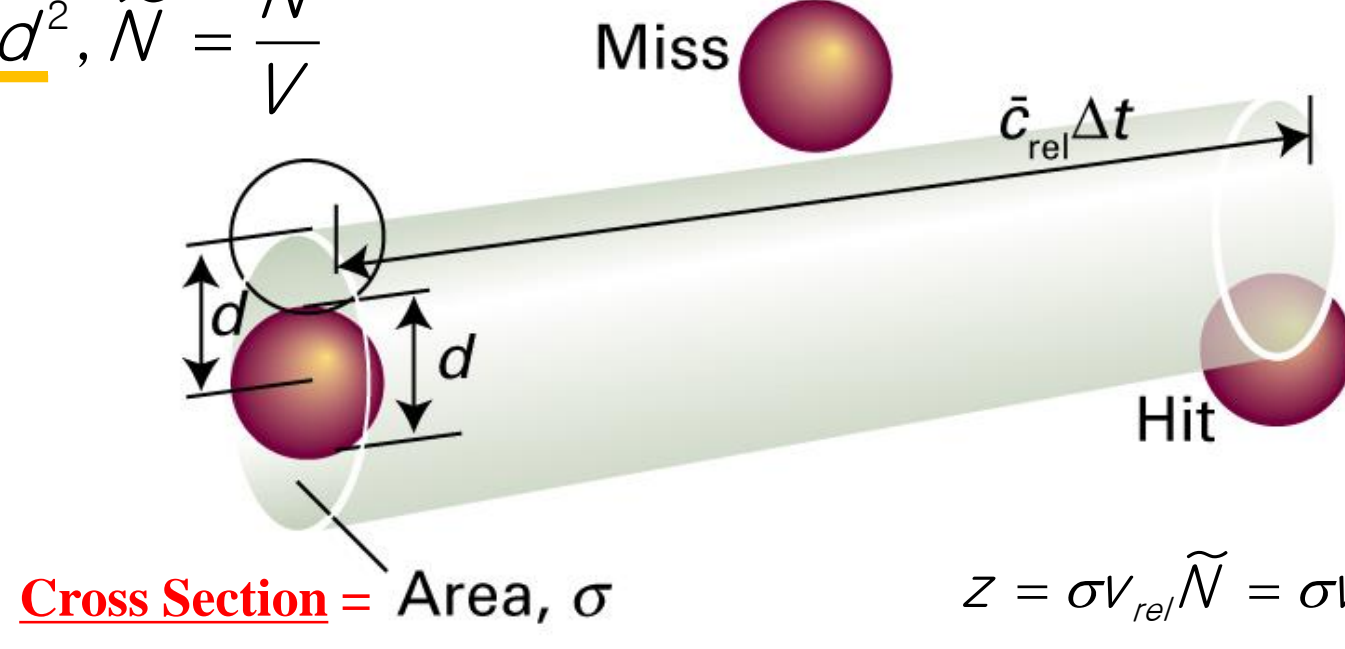
Selector

**Fig. 1.B.5**

## Velocity Selector = Time-of-Flight Measurement

The molecules are produced in the source (which may be an oven with a small hole in one wall), and travel in a beam towards the rotating disks. Only if the speed of a molecule is such as to carry it through each slot that rotates into its path will it reach the detector. Thus, the number of slow molecules can be counted by rotating the disks slowly, and the number of fast molecules counted by rotating the disks rapidly.

**$z^{-1} = \tau$ : Collision Time**

$$\sigma V_{rel} \, \Delta t = V / N$$

$$\sigma = \pi d^2, \quad \widetilde{N} = \frac{N}{V}$$

Miss

$\bar{c}_{rel}\Delta t$

(1.B.11a)
(1.B.11b)
(1.B.12)
(1.B.13)

$d$

$d$

Hit

**Cross Section** = Area, $\sigma$

$$z = \sigma V_{rel}\widetilde{N} = \sigma V_{rel}\frac{N}{V} = \frac{\sigma V_{rel} p}{kT}$$

$$\text{Mean free path } \lambda = \frac{V_{rel}}{z} = \frac{kT}{\sigma p}$$

**Figure 1.B.9**

In an interval $\Delta t$, <u>a molecule of diameter $d$</u> sweeps out a tube of diameter $2d$ and length $v_{rel}\Delta t$ . As it does so, it encounters other molecules with centers that lie within the tube, and each such encounter counts as one collision. In practice, the tube is not straight, but changes direction at each collision. Nevertheless, the volume swept out is the same, and this straightened version of tube can be used as a basis of the calculation.

$z^{-1} = \tau$ : **Collision Time**

$$v_{rel} = \sqrt{2}v_{mean} = \sqrt{2}\langle v \rangle \sim \langle v \rangle$$

**relative speed ≈ mean speed ≈ $v_{rms}$**

The **mean free path** $\lambda$,

$$\lambda = \frac{\langle v_{rel} \rangle}{Z} = \frac{1}{\sigma\left(\dfrac{N}{V}\right)} \qquad Z = \langle v_{rel} \rangle \sigma\left(\frac{N}{V}\right)$$

For a perfect gas,

$$\lambda = \frac{1}{\sigma\left(\dfrac{p}{kT}\right)} = \left(\frac{1}{\sigma}\right)\left(\frac{kT}{p}\right) \qquad \textbf{(1.B.12)}$$

The mean free path is <u>inversely proportional to the pressure</u>.

$v \approx 500$ **m/s**     **at 300 K**

$v \tau \approx 500$ **nm ($\tau \approx 1$ ns)**   **at 1 atm + 300 K**

$v \tau \approx 1$ **cm**    **at $10^{-5}$ atm + 300 K**
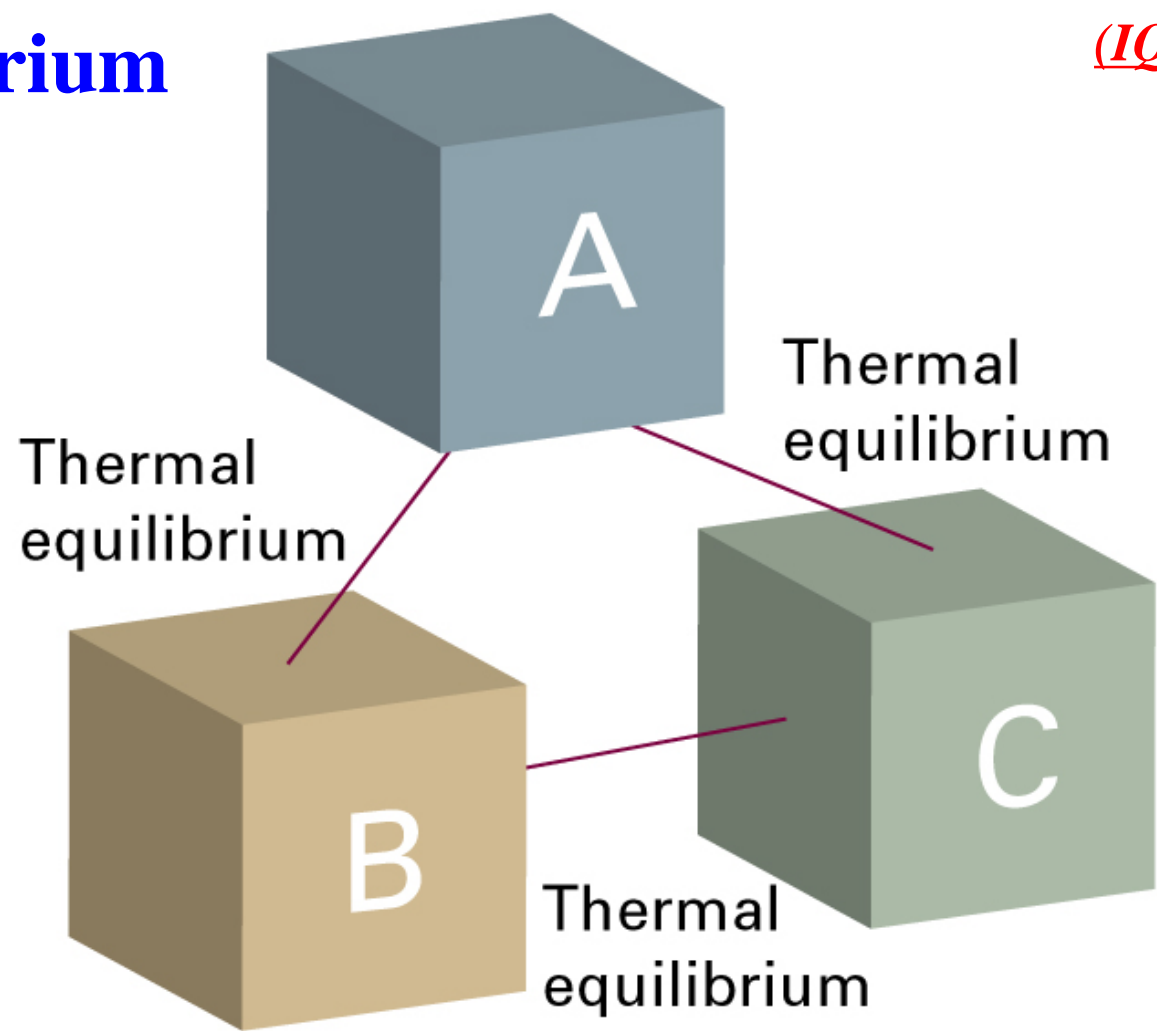
**Evaporation (in Vacuum) - reproducibility**
    **or**
**Wet Chemistry - cost**

# **Thermal Equilibrium**

The experience summarized by **the Zeroth Law of Thermodynamics**:
If an object A is in thermal equilibrium with B, and if B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

# 1.C. Real Gases

## 1.C.1. Intermolecular Forces

Pairwise potential function, $U(r)$, which gives the potential energy of the pair as a function of the distance ($r$) between their centers.

$$F = -\frac{dU}{dr}$$

At long range, a weak attractive force between the molecules

$$\rightarrow F \propto -\frac{1}{r^n}$$

At short range, the force becomes very strongly repulsive. A number of semi-empirical potentials have been proposed and used. The ability of a proposed potential to fit a variety of data over a range of temperatures with the set of parameters is an indicator of generality.
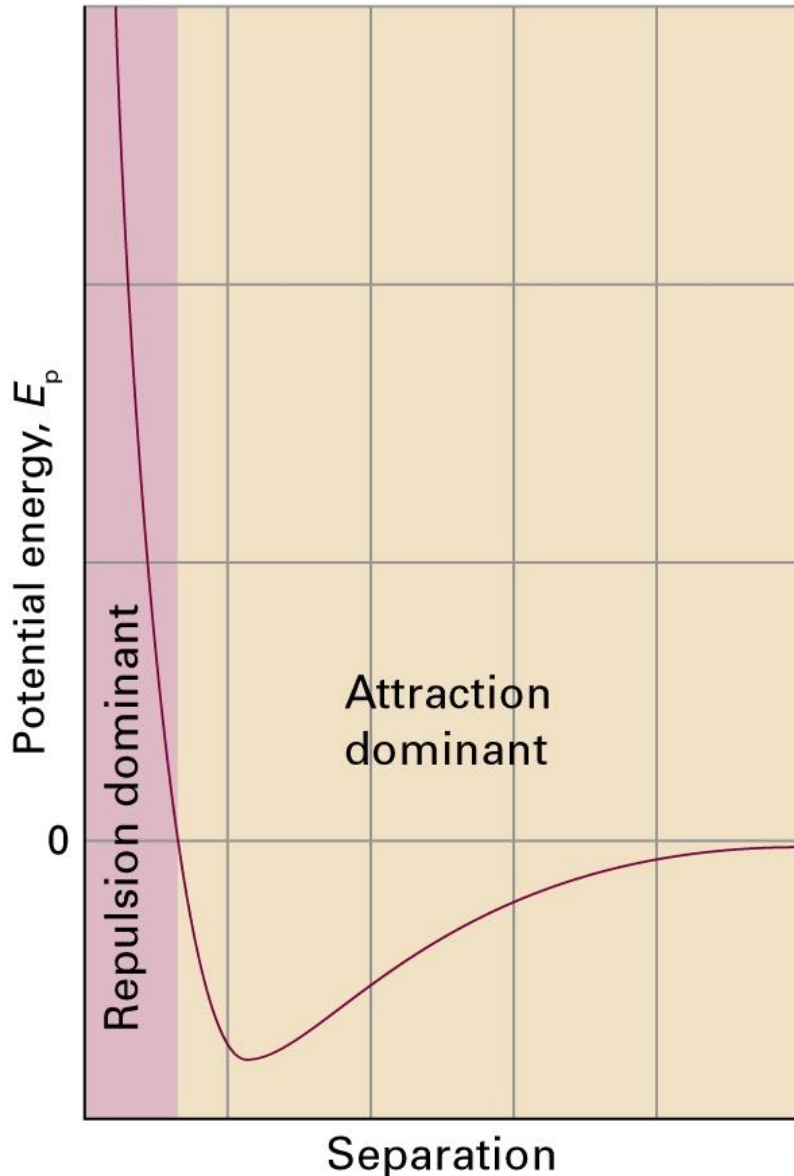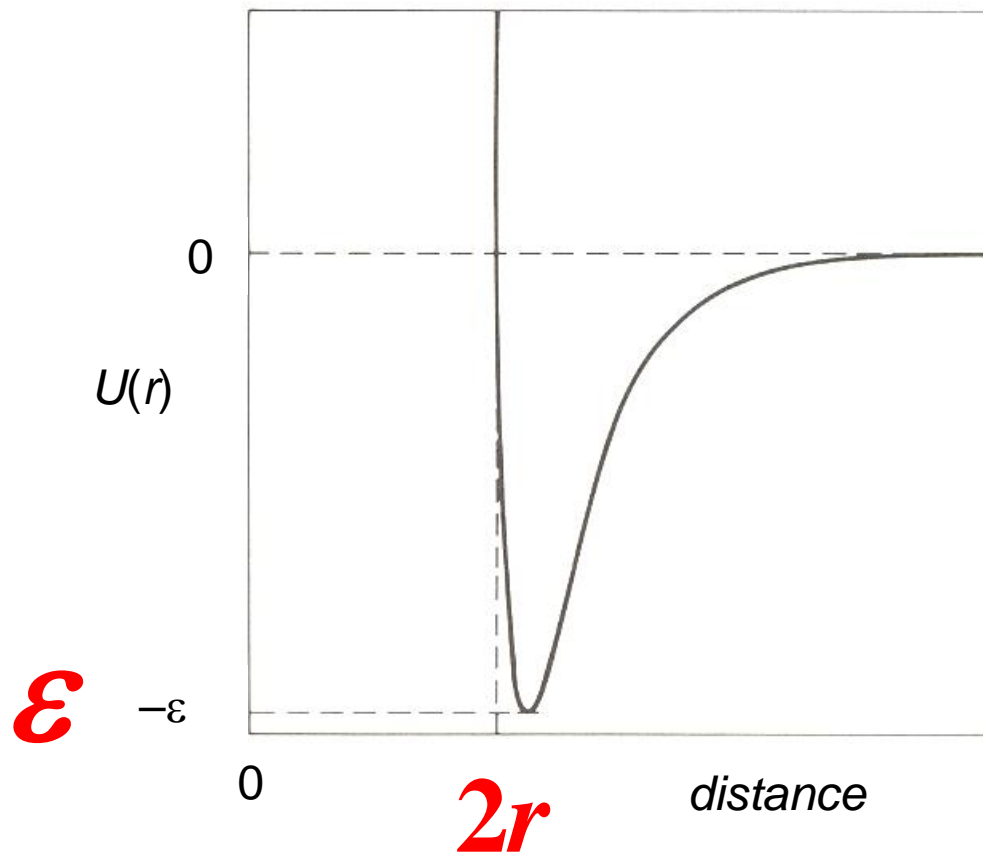
**Figure 1.C.1**

The variation of the potential energy of two molecules on their separation.

High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances.
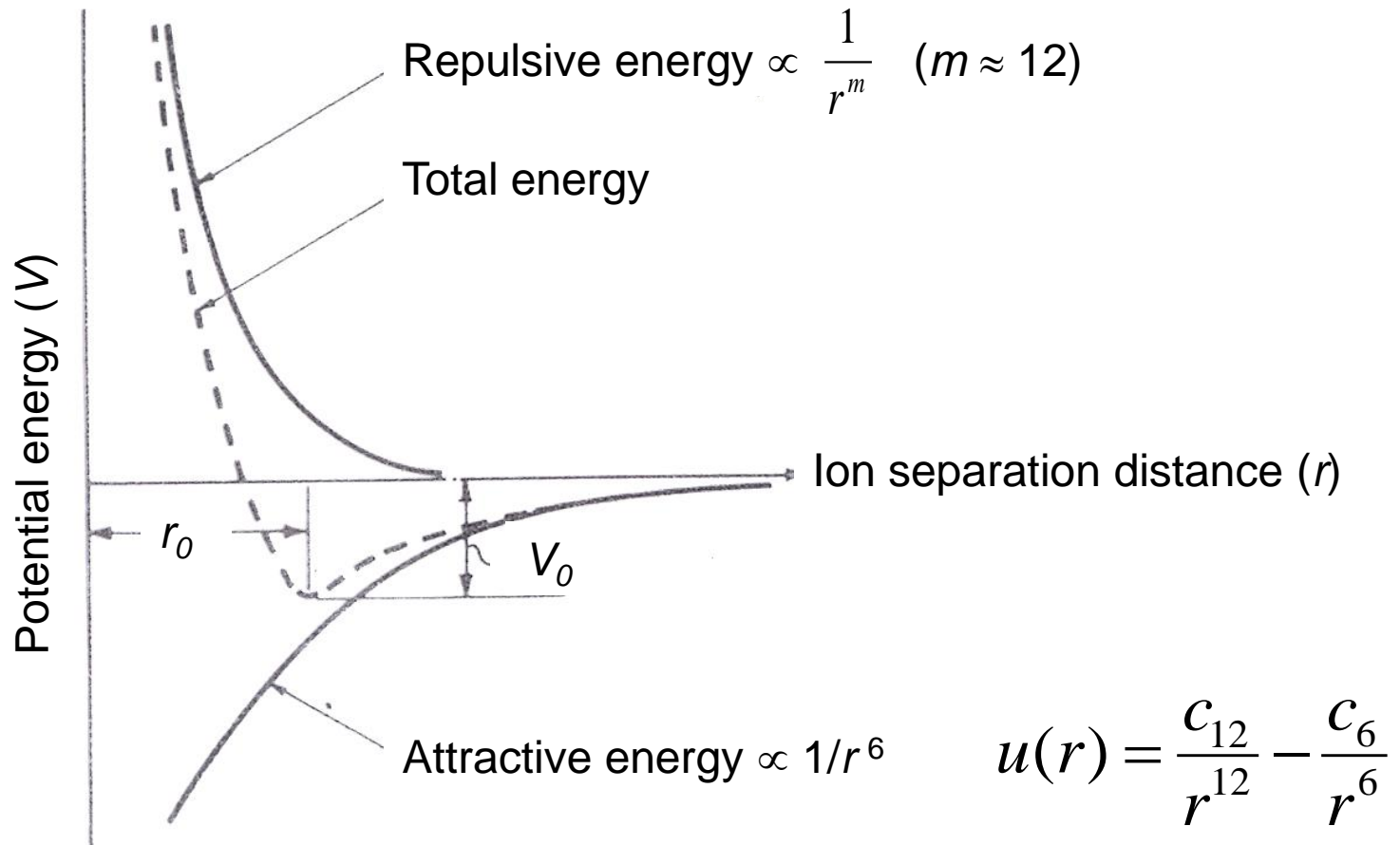
At intermediate separations, where the potential energy is negative, the attractive interactions dominate.

At large separations (on the right), the potential energy is zero and there is negligible interaction between the molecules.

**~Figure 1.C.1**

The intermolecular potential $U(r)$. The potential is a function of the distance between the centers of the molecule. This figure illustrates two parameters ($2r$), which is the **distance between the centers of the molecules** where the potential curve crosses zero, and the well-depth parameters ($\varepsilon$), which is the **depth of the potential well** at its minimum.

Repulsive energy $\propto \dfrac{1}{r^m}$ $(m \approx 12)$

Total energy

Ion separation distance ($r$)

Potential energy ($V$)

$r_0$

$V_0$

Attractive energy $\propto 1/r^6$

$$u(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6}$$

**~Fig. 1.C.1**
**Energy vs. separation distance for two atoms (or two oppositely charged ions).**

# 1.C.2. The van der Waals Equation  ≈  *Real Gas*

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

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

Ideal gas:  1. The size of molecule is negligible.

2. The interactions are negligible.

$V_m$ = *molar volume*

(1.C.5b)

$a, b$ : empirical constants that are characteristic of the particular force.

$a \rightarrow$  At finite concentrations, molecules will have **attractive forces** which will reduce the pressure.

$b \rightarrow$  The volume in the ideal gas law should not be the volume of the container, but the **volume available** to a molecule for kinetic movement.

# **Magnitude of *b* by Volume**



$2r$
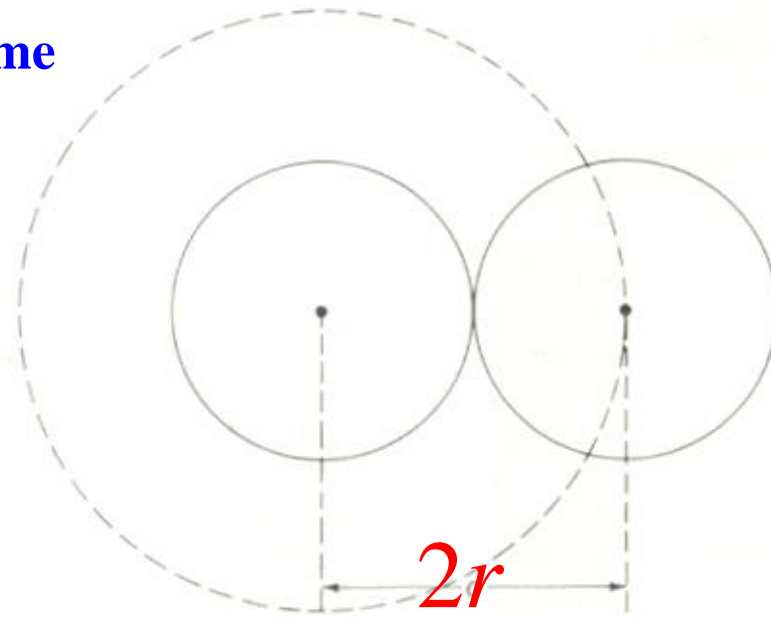
Excluded volume: **A sphere of diameter 2*r*** creates an excluded volume, which is a sphere of radius *r*, into which the center of another sphere of the same size **cannot penetrate**.

The excluded volume per **pair** of spheres: $\dfrac{4\pi(2r)^3}{3}$ .

[Justific. 1.C.1]

The excluded volume is $b = 4(4\pi\dfrac{r^3}{3})N_A$ for $N_A$ molecules.

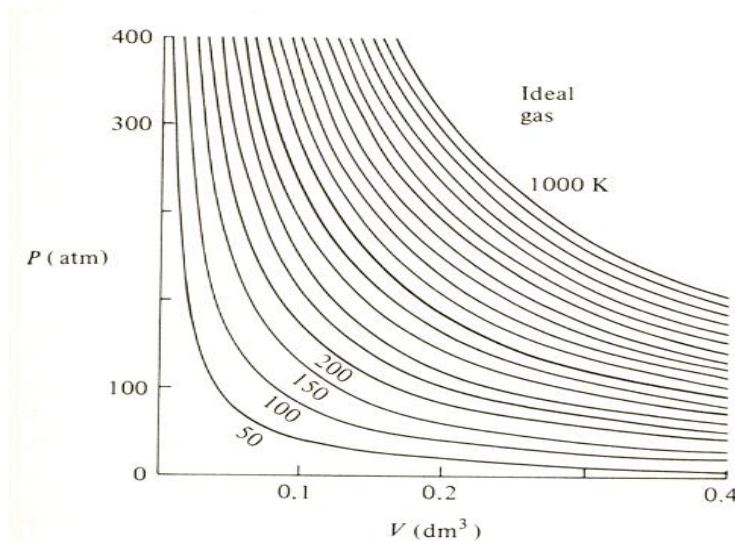$\underbrace{[\qquad\qquad\qquad]}_{\textit{per atom}}$

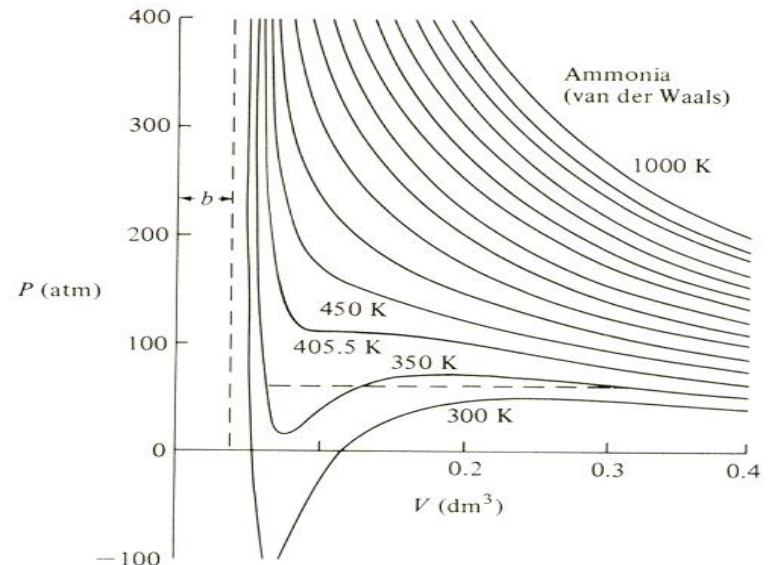# *P* - V Dependence at Different Temperatures

Gas isotherms:

Comparison of the isotherms of an ideal gas to that predicted by the van der Waals equation for ammonia.

An ideal gas will not condense at any temperature.

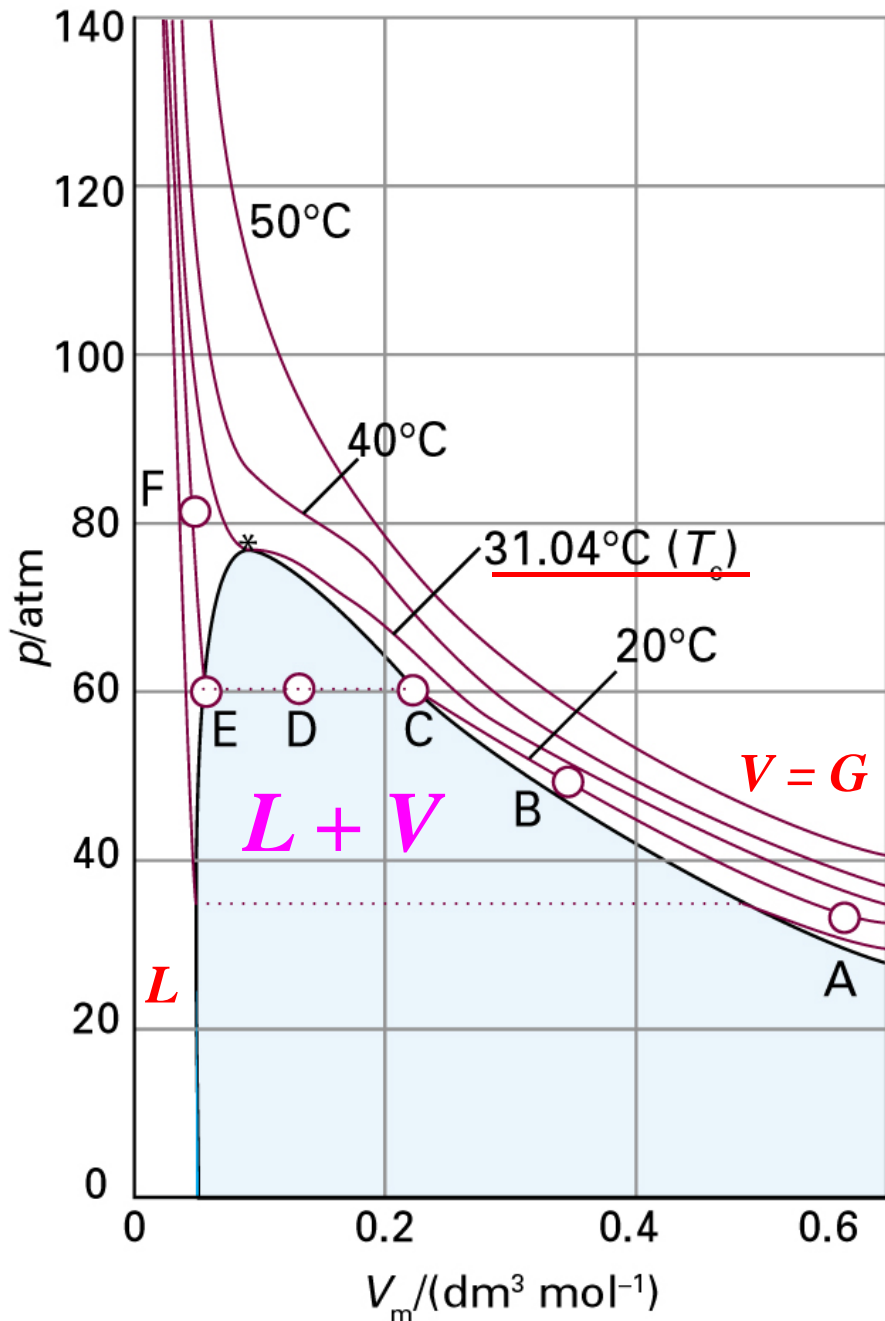**Ideal Gas**  **Ammonia (van der Waals)**
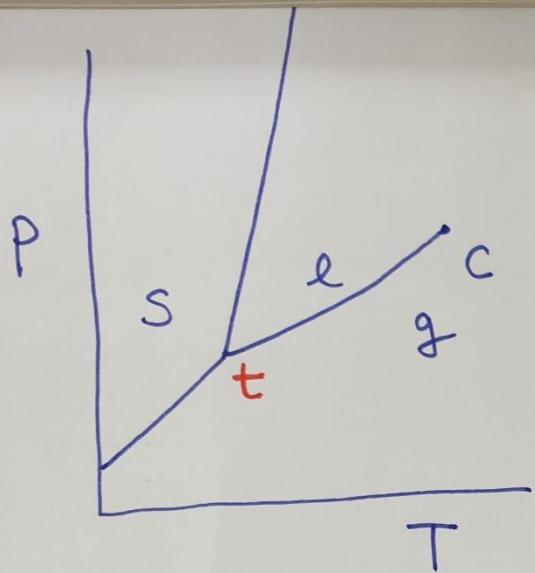
**Figure 1.C.2**
Experimental isotherms of carbon dioxide ($CO_2$) at several temperatures.

The **<u>critical isotherm *</u>**, the isotherm at the critical temperature, is at 31.04°C.  The critical point is marked with a star.

**dry ice = solid of $CO_2$**
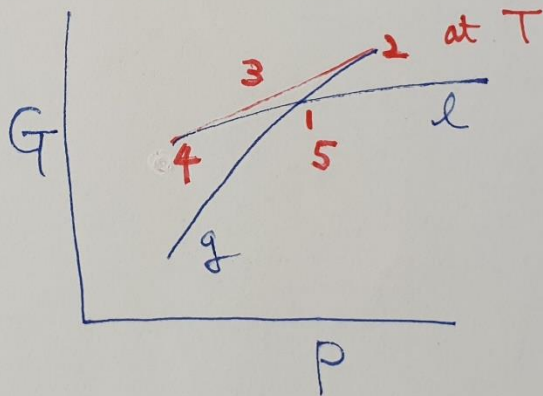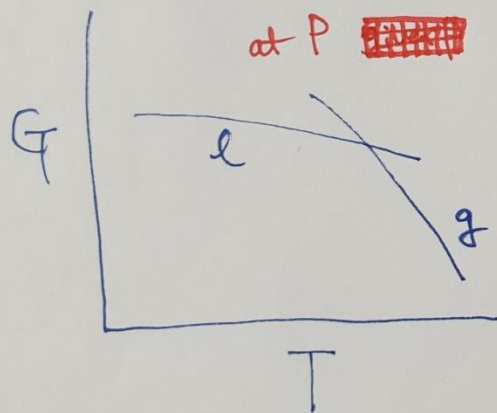
**Critical Point:  7.38 MPa  &   31.0°C**

**Triple Point:    0.52 MPa  & −56.6°C**

P

S    ℓ    C

t

g

T

Critical point (continuous transformations)

Triple point: 3 phases coexist.

P

ℓ

5

4

3

2

1

g

O

V

G

at P

ℓ

g

T

G

3

2   at T

4

1

5

ℓ

g

P
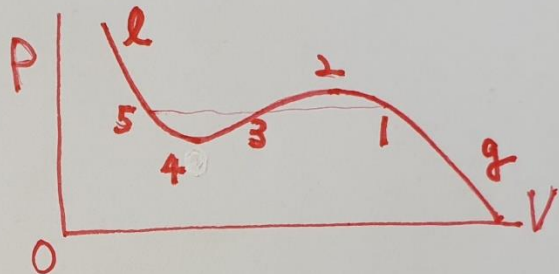
$$dG = -SdT + VdP + \sum \mu_i dN_i$$

$$G(P) = \int V dP$$

Equilibrium / Metastable / Reversible

~~Irreversible~~

**~Figure 1.C.7**

Van der Waals isotherms at several values of $T/T_c$.

The van der Waals loops are replaced by horizontal straight lines.

The critical isotherm is the isotherm for $T/T_c = 1$.
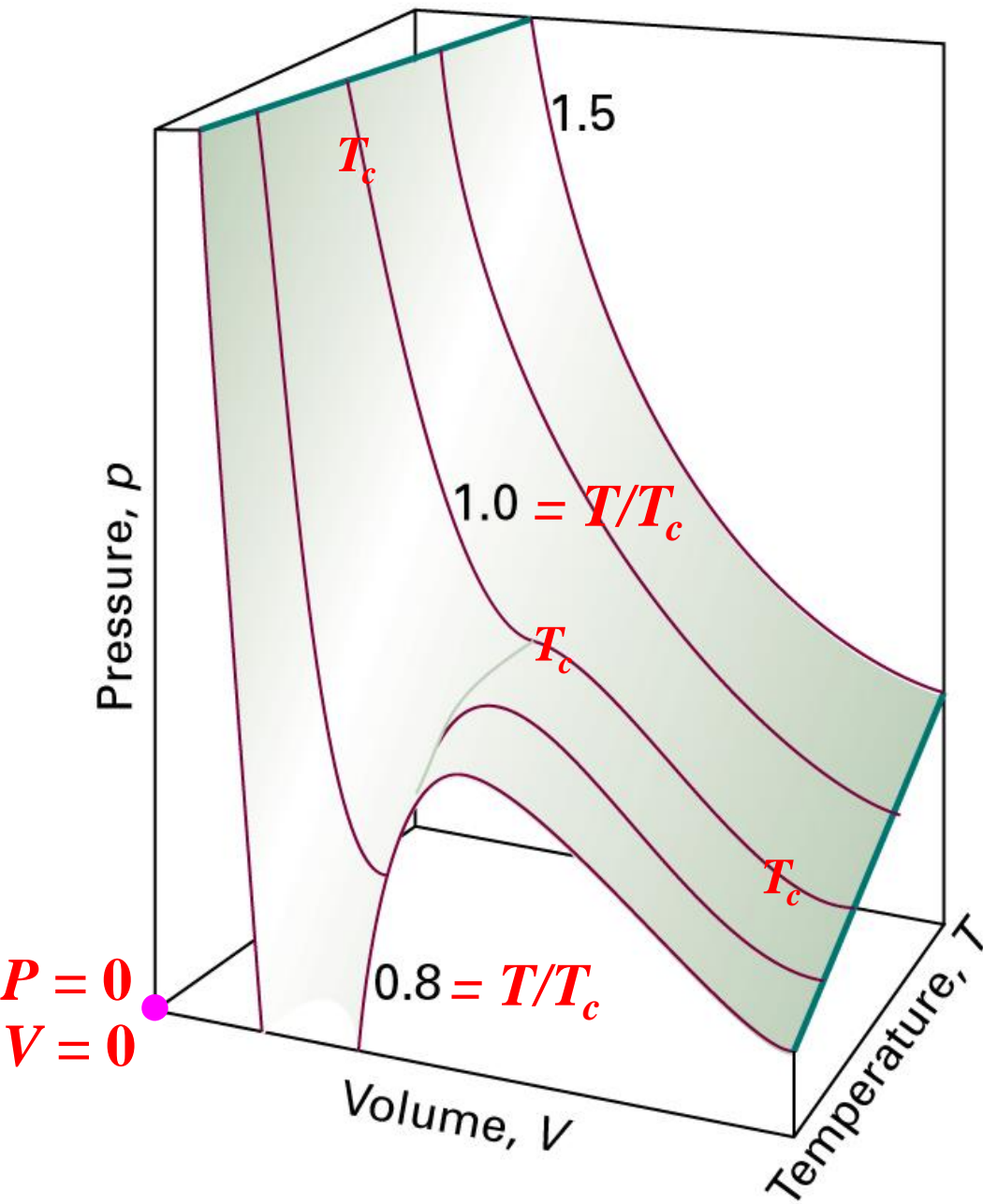
**Figure 1.C.7**
The surface of possible states allowed by the van der Waals equation.

$P = 0$
$V = 0$

For van der Waals equation,

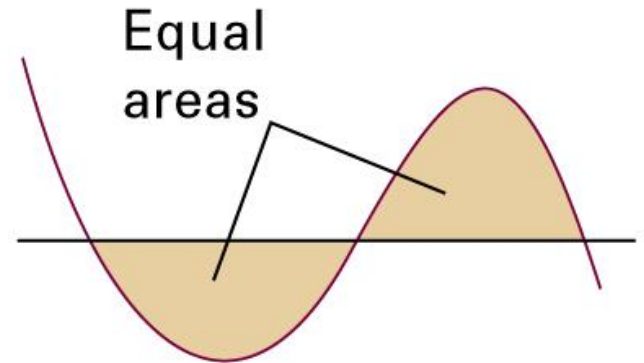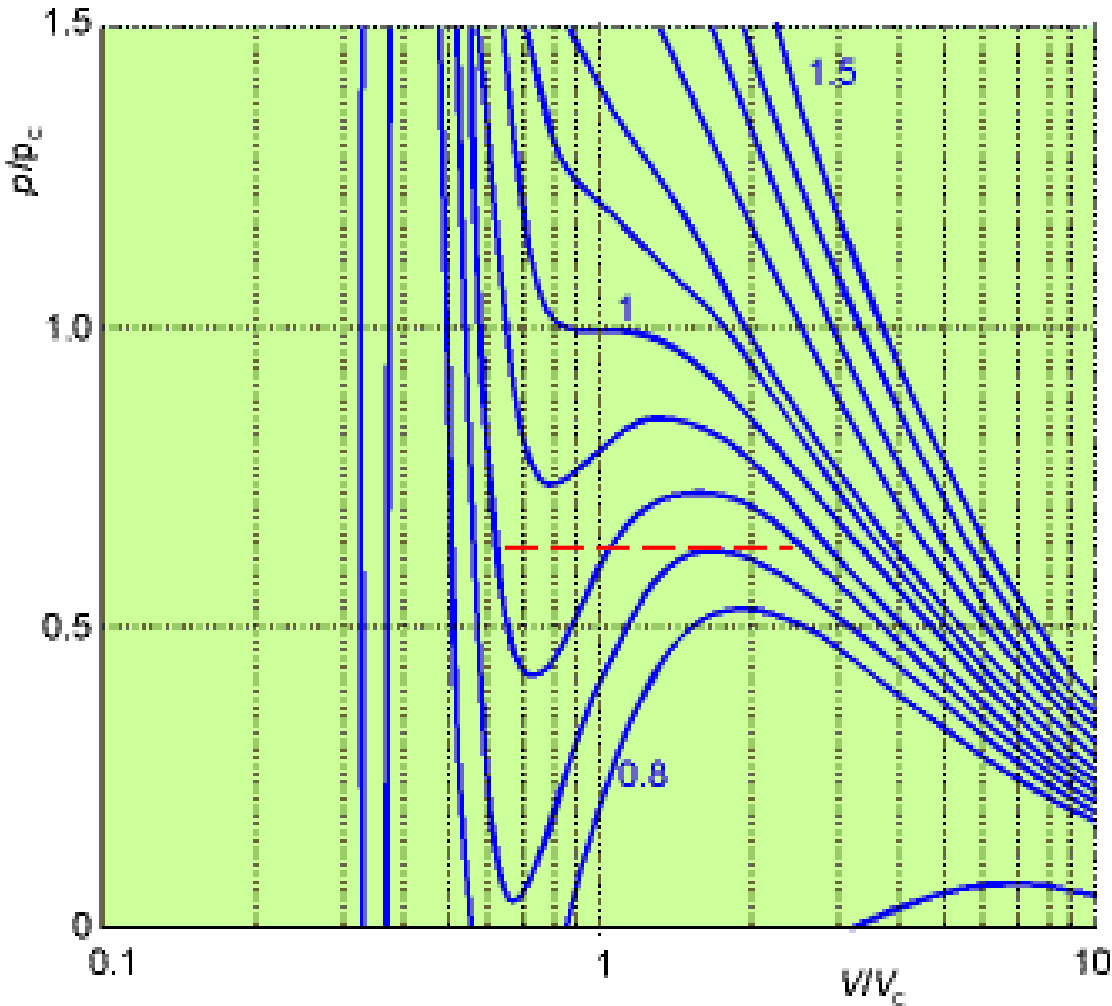$T > T_c$, somewhat realistic

$T < T_c$, the isotherms show an <span style="color:red">undulation</span> which is not at all like the observed behavior

<span style="color:blue">Reason:</span>

Van der Waals equation $\rightarrow$ cube in volume

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$V_m^3 - \left(\frac{RT}{p} + b\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \left(\frac{ab}{p}\right) = 0$$

For **any choice of $T$ and $p$**, there will be three values of the volume which will, mathematically, satisfy the van der Waals equation.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$V_m^3 - \left(\frac{RT}{p} + b\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \left(\frac{ab}{p}\right) = 0$$

A cubic equation $\rightarrow$ three roots

$T > T_c \rightarrow$ one real, two complex

$T = T_c \rightarrow$ all three roots: real and equal

$T < T_c \rightarrow$ all three roots: real and unequal

Horizontal line is drawn through the undulation with equal areas above & below:

Interpreted as the vapor pressure of the liquid. (Maxwell construction)

**Why?** (derivation on ppt 1-36)

[Later]

$$dG(T, p, n_j) = -SdT + Vdp + \sum_i \mu_i dn_i$$

*Reversible*
*Equilibrium*
*Metastable*

# Critical Behavior of Fluids

$P$ vs. $V$ (or $P$ vs. $V_m$) for a gas at constant temperature (isotherms)



Isotherms for various temperature

$T$

$L$ or $G$

Pressure

C

$L + G$

Liquid    Gas

$L$    Two–phase region

$G = V$

Volume
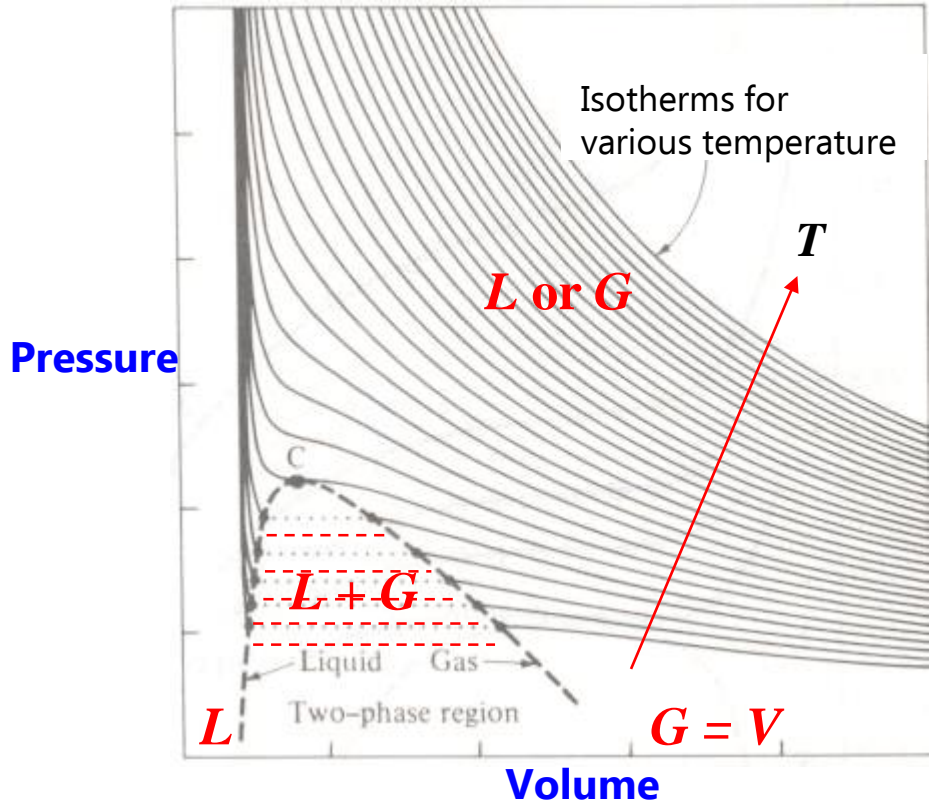
$T > T_c$

$at\ T_c$

$T < T_c$

~**Fig. 1.C.7**

At high temperatures, these are similar to the hyperbolae predicted by the <u>ideal gas law</u>.

At the **critical temperature**, the isotherm has a <u>horizontal inflection</u> at the critical point (C).

<u>Below the critical temperature</u>, the isotherms have a horizontal segment (shown by the dotted lines) in the **two-phase region**, where both liquid and vapor are present.

Near the critical temperature, the isotherms have a nearly horizontal section.

At the critical temperature, this becomes an <u>inflection point</u> for which the slope is zero at some point − namely, the critical point ($P_c$, $V_c$, $T_c$).

- - - - - - - - - - - - - - - - - - - - - - - - -

<u>Meaning of the Horizontal Part of the Isotherms below $T_c$:</u>

- The value of the pressure at which, for a given temperature, <u>liquid and vapor phases are in equilibrium</u> (i.e., the horizontal lines) is called the **vapor pressure**.

- The total volume of the <u>liquid + vapor</u> can increase <u>without a change in pressure</u>.

- If there are two phases in the container, <u>compression</u> will cause more vapor to condense into the higher-fraction liquid, but <u>at the same pressure</u>.
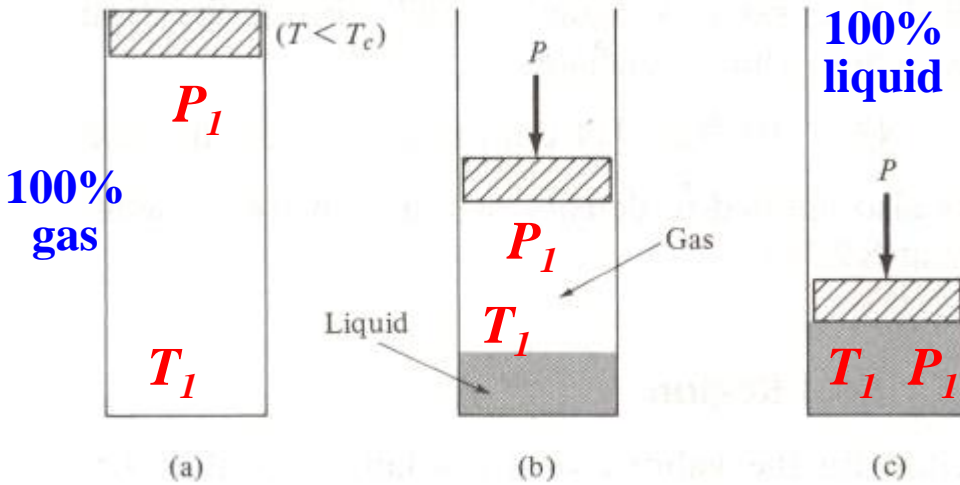
at $T_1 < T_c$
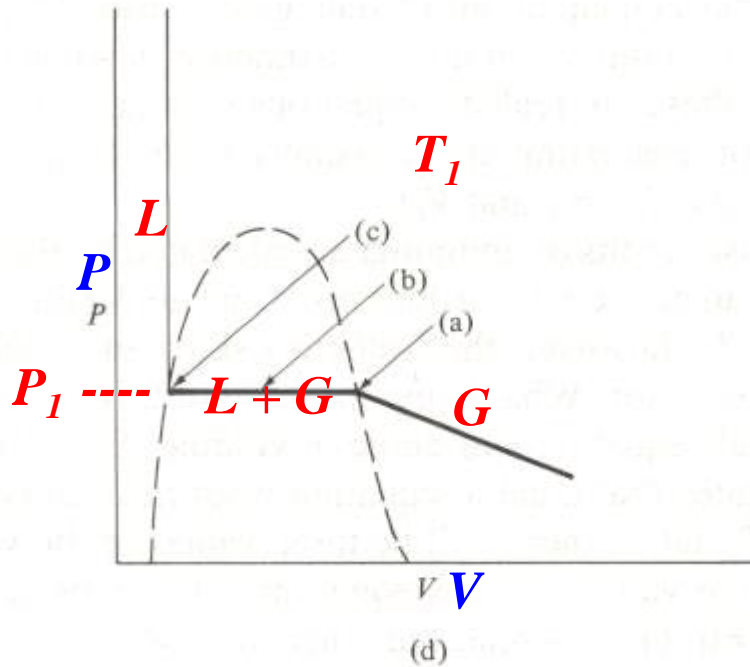


The isothermal compression of a gas (below its critical temperature) will, at the *P-V* point (a), cause the condensation of a liquid.

Further reduction of volume will cause more gas to condense, but the pressure will not change. This is the ***vapor pressure* of liquid at this temperature**.

At point (c), all the gas will be condensed to a liquid, and further reduction of volume requires the compression of the liquid.

# 1.4(b). Evaluation of Gas Constants from the Critical Data

At the critical temperature, the curve has an inflection at which the gradient and curvature are zero.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \longleftrightarrow \quad V_m^3 - \left(\frac{RT}{p} + b\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \left(\frac{ab}{p}\right) = 0$$

*1st derivative*

$$\frac{dp}{dV_m} = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$$

*2nd derivative*

$$\frac{d^2 p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0$$

$\left.\right\}$ at $T = T_c,\ p = p_c,\ V_m = V_{m,c}$

$$V_{m,c} = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27bR}$$

**(1.C.6)**

**Table (1.C.4)**

# 1.C.2(c). The Principle of Corresponding States

- The He and $CO_2$ gases look very different in their behavior <u>at any given temperature and pressure</u>.

- However, if we compare them, each <u><span style="color:red">by its critical point</span></u>, their compression factors are nearly the same.

He: $T_c$=5.3 K,  $p_c$=2.26 atm,  $V_c$=57.7 cm$^3$/mol  $\rightarrow$  $Z_c$=0.300

$CO_2$: $T_c$=304.2 K,  $p_c$=73.0 atm,  $V_c$=95.6 cm$^3$/mol  $\rightarrow$  $Z_c$=0.280

<span style="color:red">The law of corresponding states</span> demonstrates that the compression factor (and many other intensive properties) of any gas can be written as a

## <span style="color:red">universal function</span> of the <u>reduced variables</u>:

$$T_r = \frac{T}{T_c}, \quad p_r = \frac{p}{p_c}, \quad V_r = \frac{V_m}{V_{m,c}}$$

Write the $p$, $V_m$ and $T$ of van der Waals equation in terms of the reduced variables, and then express the latter in terms of the relations in eqs:

$$p_c = a/27b^2, \quad V_{m,c} = 3b, \quad T_c = 8a/27bR.$$

$$p = p_r p_c = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{RT_r T_c}{V_r V_{m,c} - b} - \frac{a}{V_r^2 V_{m,c}^2}$$

$$p_r p_c = p_r \frac{a}{27b^2} = \frac{RT\left(\dfrac{8a}{27bR}\right)}{3bV_r - b} - \frac{a}{V_r^2(9b^2)} = \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2 V_r^2}$$

$$\therefore p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

**(1.C.9)**

**Meaning**

These have the same form as the original equation. However,

**the constants $a$ and $b$, which differ from gas to gas, have disappeared.**

$$T_r = \frac{T}{T_c}, \quad p_r = \frac{p}{p_c}, \quad V_r = \frac{V_m}{V_{m,c}}$$

$$Z(p,T) \equiv PV / Nk_BT$$

$$= V^{\,real} / V^{\,ideal}$$

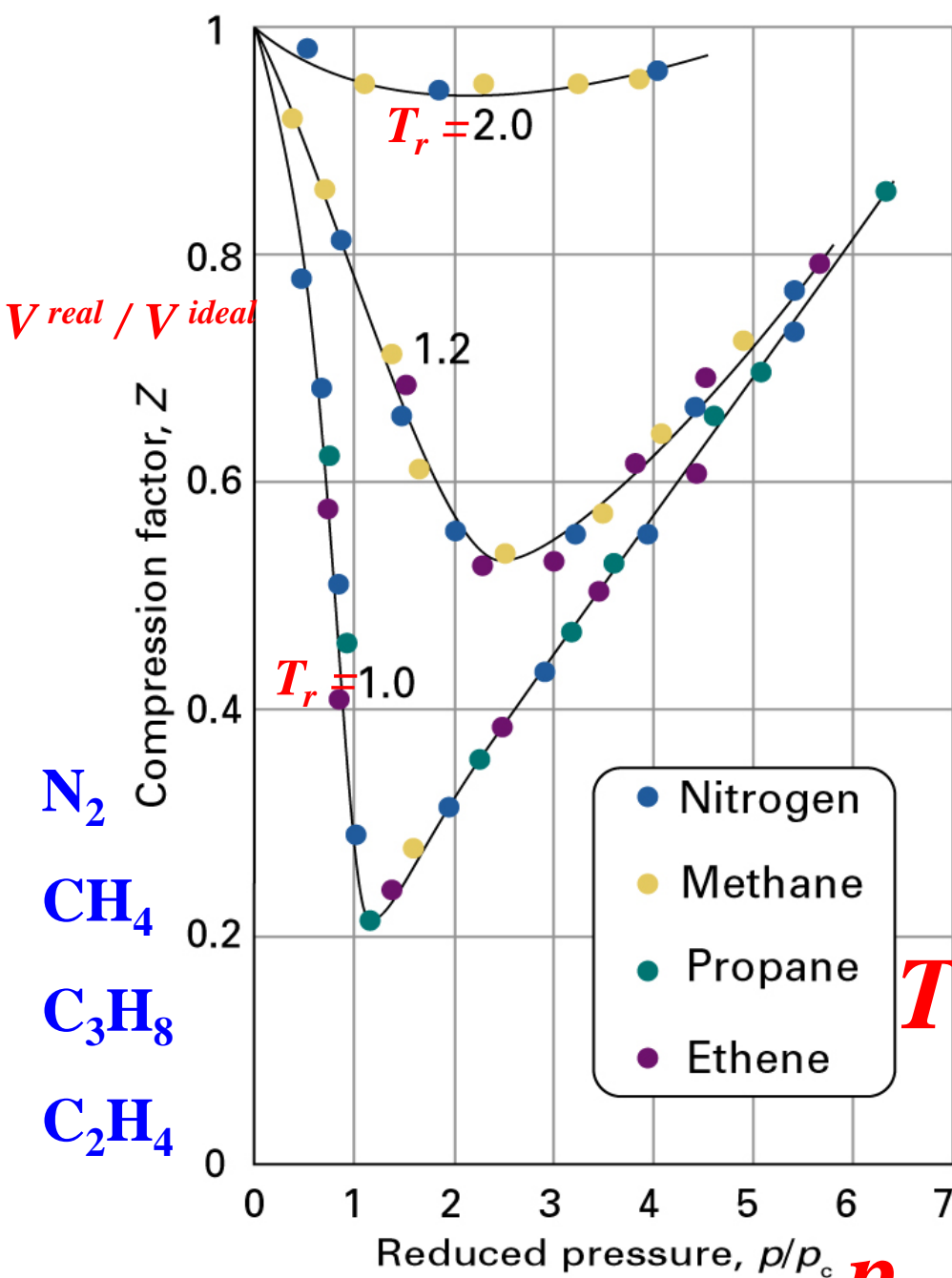$V^{\,real} / V^{\,ideal}$

**Figure 1.C.9**

The compression factors of four gases plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. **The use of reduced variables organizes the data onto a single curve.**

$T_r = 2.0$

$1.2$

$T_r = 1.0$

$N_2$

$CH_4$

$C_3H_8$

$C_2H_4$

- Nitrogen
- Methane
- Propane
- Ethene

$$T_r = T / T_c$$

$$p_r = p / p_c$$

## 1.C.1(a). The Compresssion Factor
## 1.C.1(b). The Virial Series

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Define the compression factor:

$$p\, V_m = R\, T\, Z \qquad \left( \frac{n}{V} = \frac{1}{V_m} \right)$$

$$Z\,(p,T) \equiv p\, V_m\, /\, R\, T$$

$$= V_m\, /\, V_m^{ideal}$$

For ideal gas, $\quad Z \to 1$

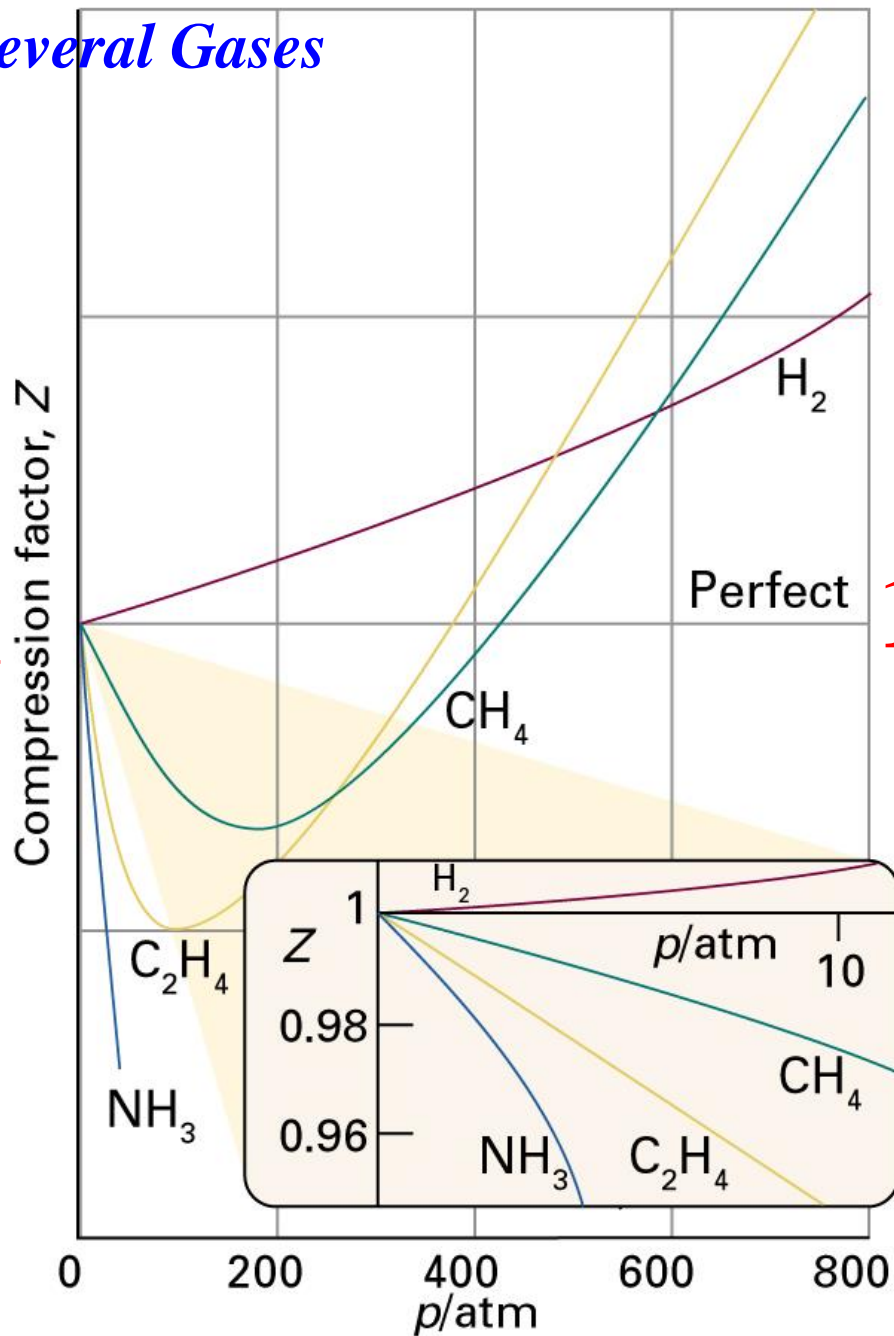(1.C.2)

For real gas, $\quad \underline{p \to 0, Z \to 1}$

$\therefore$ We might represent $Z$ as a power series in the mole concentration:

$$Z = 1 + B\left(\frac{n}{V}\right) + C\left(\frac{n}{V}\right)^2 + D\left(\frac{n}{V}\right)^3 + E\left(\frac{n}{V}\right)^4 + \cdots \qquad \text{(1.C.3b)}$$

$B = B(T)$ : the second virial coefficient

$C = C(T)$ : the third virial coefficient

# *Several Gases*



$$Z\,(p,T) \equiv p\,V_m\,/\,R\,T$$

$$= V_m\,/\,V_m^{ideal}$$

**Figure 1.C.3**
The variation of the compression factor $Z = pV_m/RT$ with pressure for several gases <u>at 0°C</u>. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves **approach 1 as $p \to 0$**, they do so with different slopes.

# Estimation of Virial Coefficients

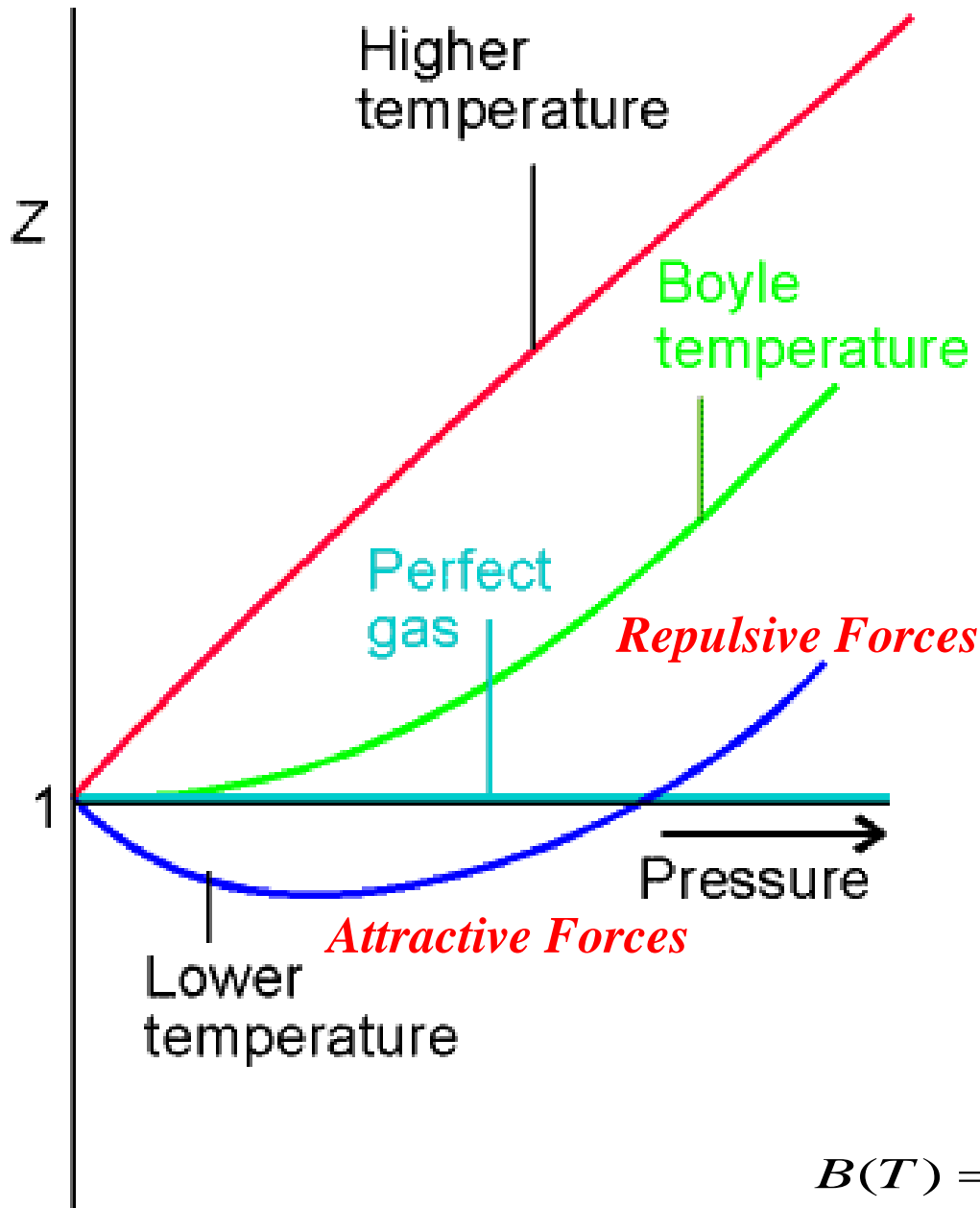The virial coefficients can be related to the <u>van der Waals constants</u>.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad \left( \frac{n}{V} = \frac{1}{V_m} \right)$$

$$Z = 1 + B\left(\frac{n}{V}\right) + C\left(\frac{n}{V}\right)^2 + D\left(\frac{n}{V}\right)^3 + \cdots$$

$$B(T) = b - \frac{a}{RT}, \quad C = b^2, \quad D = b^3$$

$$Z(p,T) \equiv p\, V_m / R\, T$$
$$= V_m / V_m^{ideal}$$

$$Z\,(p,T) \equiv p\,V_m\,/\,R\,T$$

$$= V_m\,/\,V_m^{ideal}$$

**Figure 1.C.4**
The compression factor approaches 1 at low pressures, but does so with different slopes. Real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

$$B(T) = b - \frac{a}{RT}, \quad C = b^2, \quad D = b^3$$

# The Boyle Temperature

For all gases, there is some temperature at which $B(T) = 0$.

Boyle temperature $\rightarrow$ the **<u>repulsive and attractive forces</u>**
**<u>cancel</u>** each other, giving nearly ideal behavior.

Example: Estimate the Boyle Temperature of $N_2$:
the actual value is <u>324 K</u>.

$$a(N_2) = 1.39 \left( dm^6 atm/mol^2 \right)$$
$$b(N_2) = 0.0391 \left( dm^3/mol \right)$$

**Table 1.C.3**

From van der Waals constants,

$$b - \frac{a}{RT_B} = 0 \qquad T_B = \frac{a}{bR}$$

$$T_B = \frac{1.39}{(0.0391)(0.08206)} = 433 \text{ K}$$

## The Lennard-Jones Potential

(See page 13)

**Second virial coefficient**

$$U(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

$$B(T) = 2\pi N_A \int_0^\infty \left(1-e^{-\frac{U}{kT}}\right)r^2 dr$$

The integral part of the equation for the second virial coefficient can be done analytically, but the solution is complicated and in the form of an infinite series.

Define a unitless distance as

$$\rho=\frac{r}{\sigma} \qquad \therefore B(T)=2\pi N_A\sigma^3\int_0^\infty\left(1-e^{-\frac{U}{kT}}\right)\rho^2 d\rho$$

Define a parameter:

$$b_0=\frac{2\pi N_A\sigma^3}{3} \quad \therefore B=3b_0\int_0^\infty\left(1-e^{-\frac{U}{kT}}\right)\rho^2 d\rho$$

For the Lennard-Jones (L–J) potential, the exponent in the integral is:

$$\frac{U}{kT} = \frac{4\left(\varepsilon/k\right)}{T}\left[\frac{1}{\rho^{12}} - \frac{1}{\rho^6}\right]$$

Note that $\varepsilon/k$ has unit of temperature, i.e., Kelvin. This suggests the use of two reduced parameters.

Define a parameter

$$\tilde{B} = \frac{B}{b_0}, \quad \tilde{T} = \frac{T}{\left(\varepsilon/k\right)}$$

$$\tilde{B} = 3\int_0^\infty \left\{1 - \exp\left[-\frac{4\left(\rho^{-12} - \rho^{-6}\right)}{\tilde{T}}\right]\right\}\rho^2 d\rho$$

Note that the reduced virial coefficient is a universal function of the reduced temperature. The integral must be evaluated numerically for each of $\tilde{T}$.

The <u>simplest assumption</u> is that of an **ideal mixture**.

     1. The sizes of different molecules are all <u>negligibe</u>.

     2. The <u>interactions</u> between any molecules <u>do not exist</u>.

Daltons's law

$$p = \sum_i p_i$$

where **$p_i$ is the partial pressure**, the pressure exerted by the individual gases.

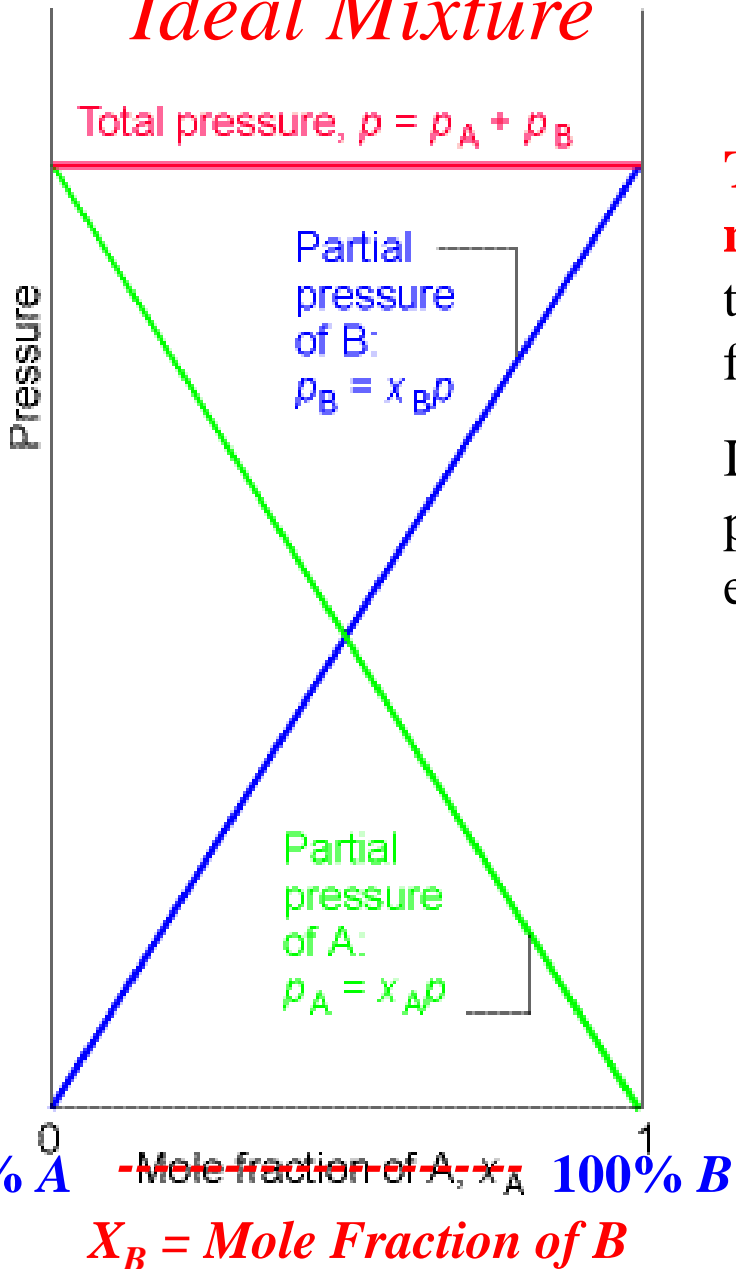The total pressure of a gas is in **proportion to the numbers of molecules** present:

$$p_i = x_i p$$

where **$x_i$ is the mole fraction**.

**(1.A.8)**
*not definition*
**textbook error**

$$x_i = \frac{n_i}{n_1 + n_2 + \cdots}, \quad \sum_i x_i = 1$$

$$p_i = f(n_i, V, T)$$

# *Ideal Mixture*

$$P_i \, V = N_i \, k_B \, T$$

Total pressure, $p = p_A + p_B$

Partial pressure of B:
$p_B = x_B p$

Pressure

Partial pressure of A:
$p_A = x_A p$

0    Mole fraction of A, $x_A$    1

**The partial pressures $P_A$ and $P_B$ of a binary mixture of [ideal (perfect) or real] gases of** total pressure *P* as the composition changes from pure *A* to pure *B*.

If the gases are <u>ideal (perfect)</u>, then the partial pressure is also the pressure that each gas would exert if it were present alone in the container.
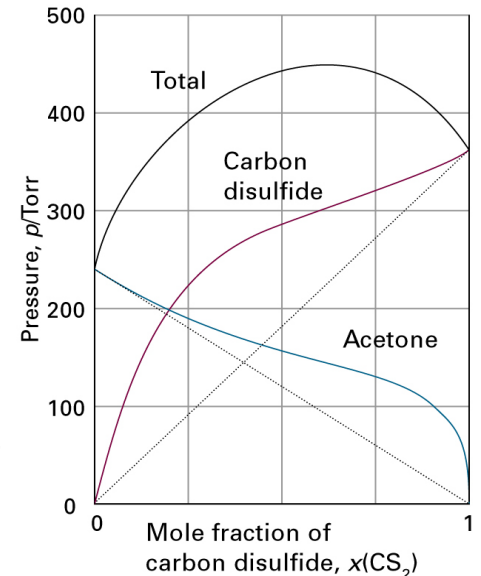
*100% A*    *100% B*

*$X_B$ = Mole Fraction of B*

*Real Mixture*

Total

Carbon disulfide

Acetone

Pressure, $p$/Torr

500 — 400 — 300 — 200 — 100 — 0

Mole fraction of carbon disulfide, $x(CS_2)$

**Figure 5A.13**

# Problems from Chap. 1

**1A.2**

**1A.5(b)    1A.8(b)    1A.9(b)**

**1A.6**

**1B.2**

**1B.2(b)    1B.3(b)    1B.6(b)**

**1B.4    1B.6**

**1C.2**