

Chapter 1. Properties of Gases

Equation of State

The physical state of a pure substance is defined 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:

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

Extensive Properties: properties proportional to the amount of material.

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

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

e.g., **temperature, pressure, diffusivity, viscosity, thermal conductivity, electrical conductivity, dielectric constant, 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.

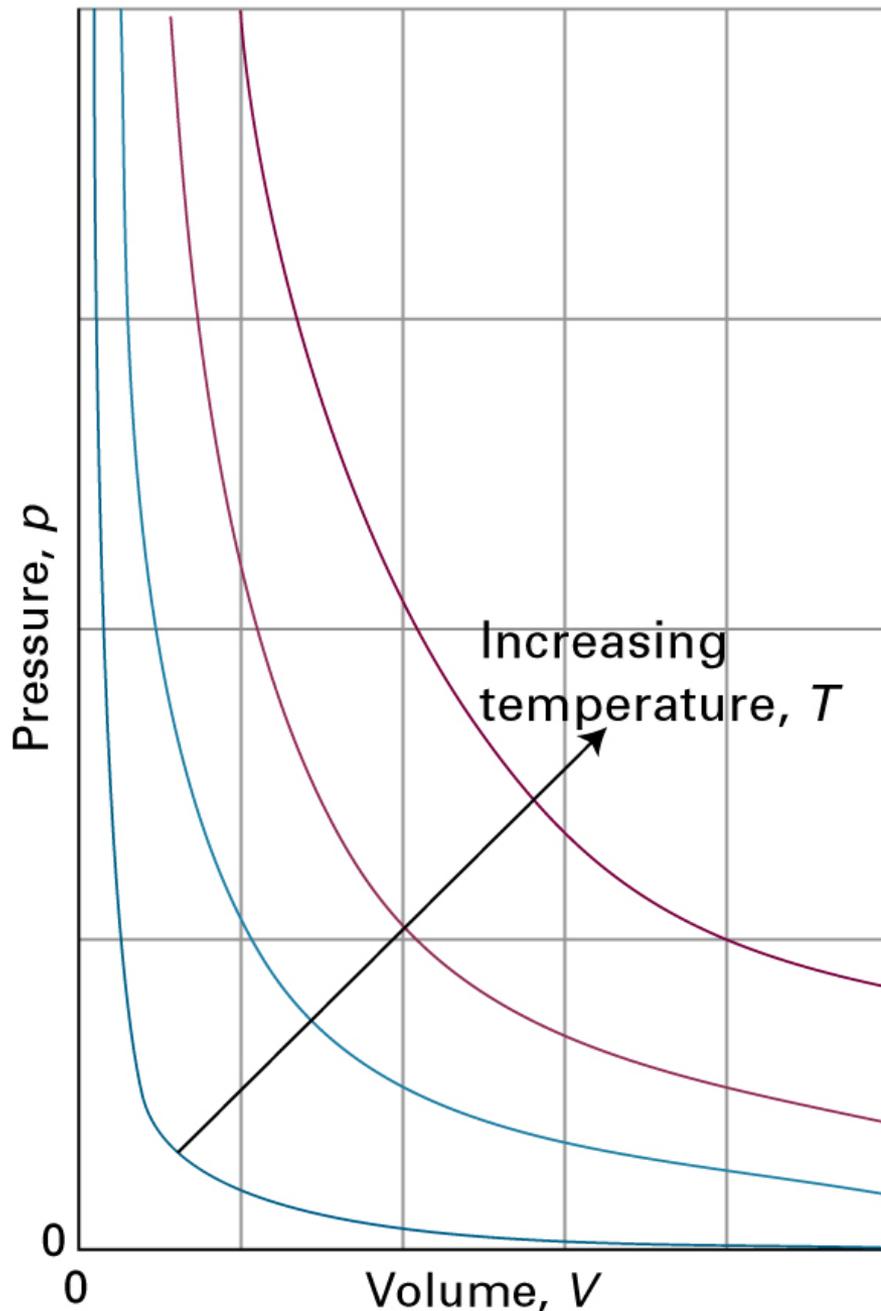
Intensive Property: $f(P, T)$ or $f(\sigma, T)$
1 Component IQ 200

Equation of state \leftrightarrow Functional dependence of any other properties on these two variables.

1A.2 The Ideal Gas Law (Perfect Gas)

- Ideal Gas: **1. The size of molecule is negligibly small.**
2. The interactions between molecules do not exist.

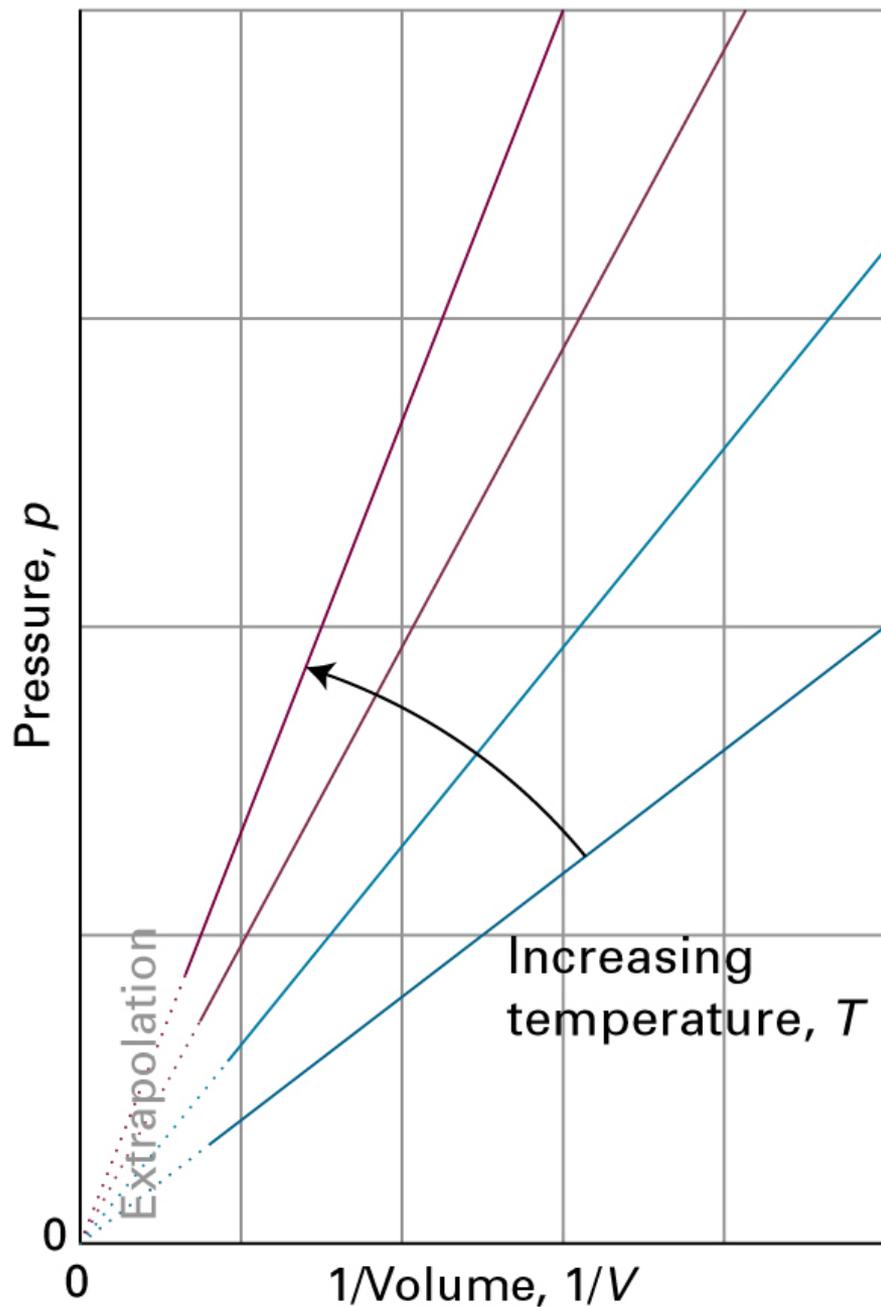
$$p V = n R T \quad p V = N k_B T$$



$$PV = nRT$$

Figure 1A.2

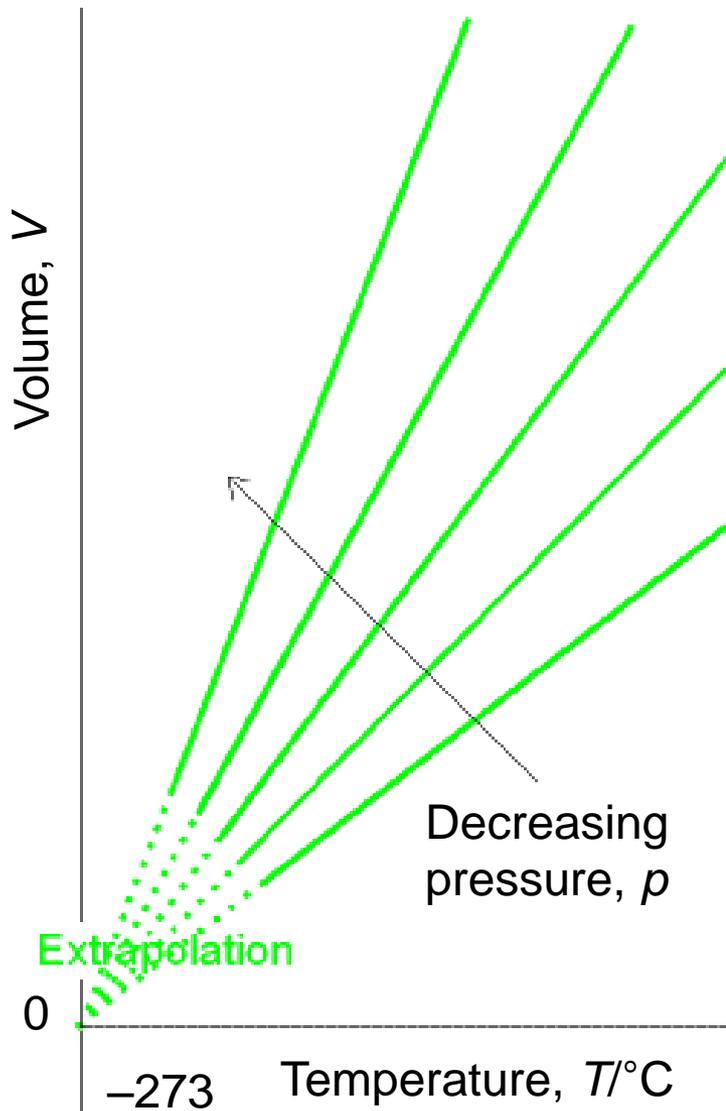
The pressure-volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an **isotherm**.



$$p = \frac{nRT}{V}$$

Figure 1A.3

Straight lines are obtained when the pressure is plotted against $1/V$.



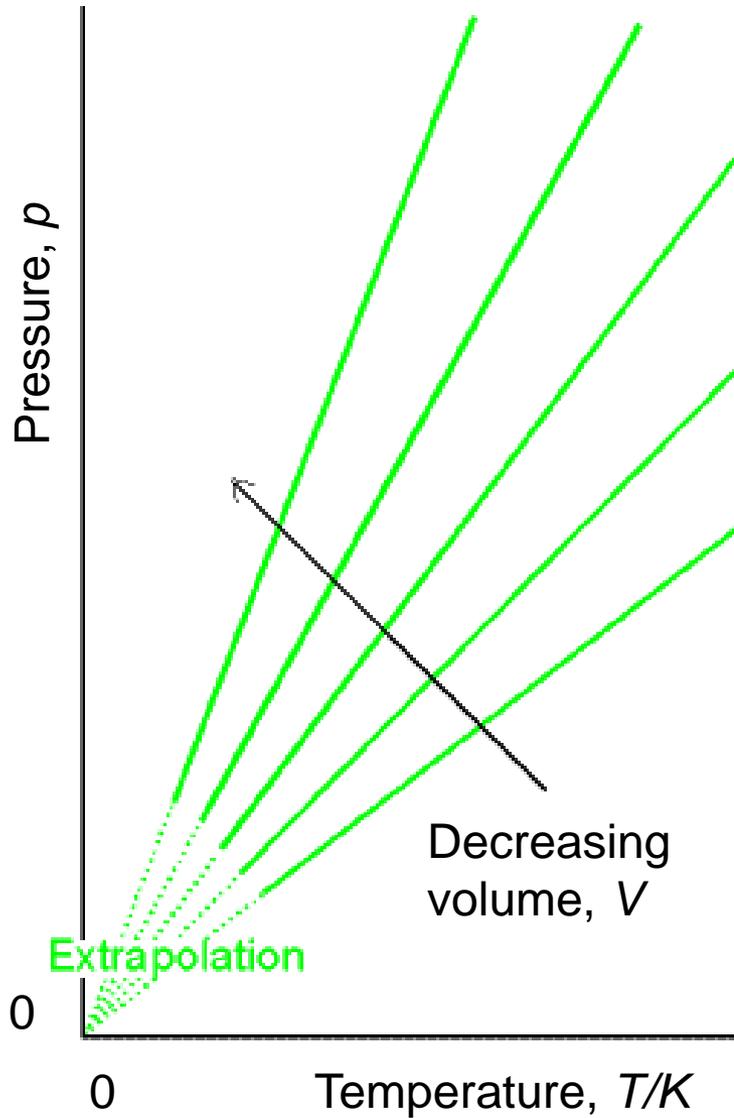
$$V = \frac{nRT}{p}$$

Figure 1A.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

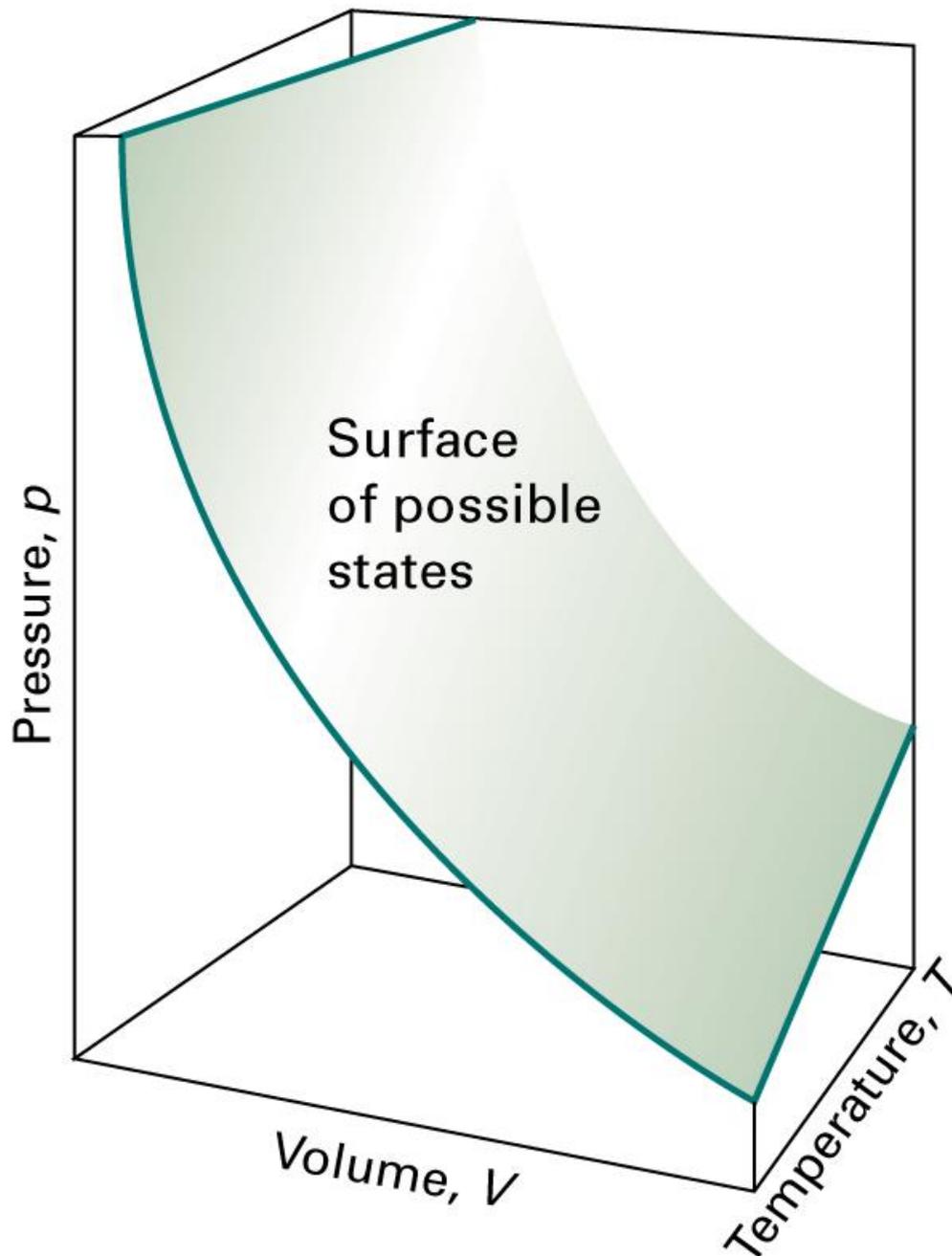


$$p = \frac{nRT}{V}$$

Figure 1A.5

The pressure also varies linearly with the temperature at **constant volume**, and extrapolates to zero at $T = 0 \text{ K}$ ($= -273.15^\circ\text{C}$).

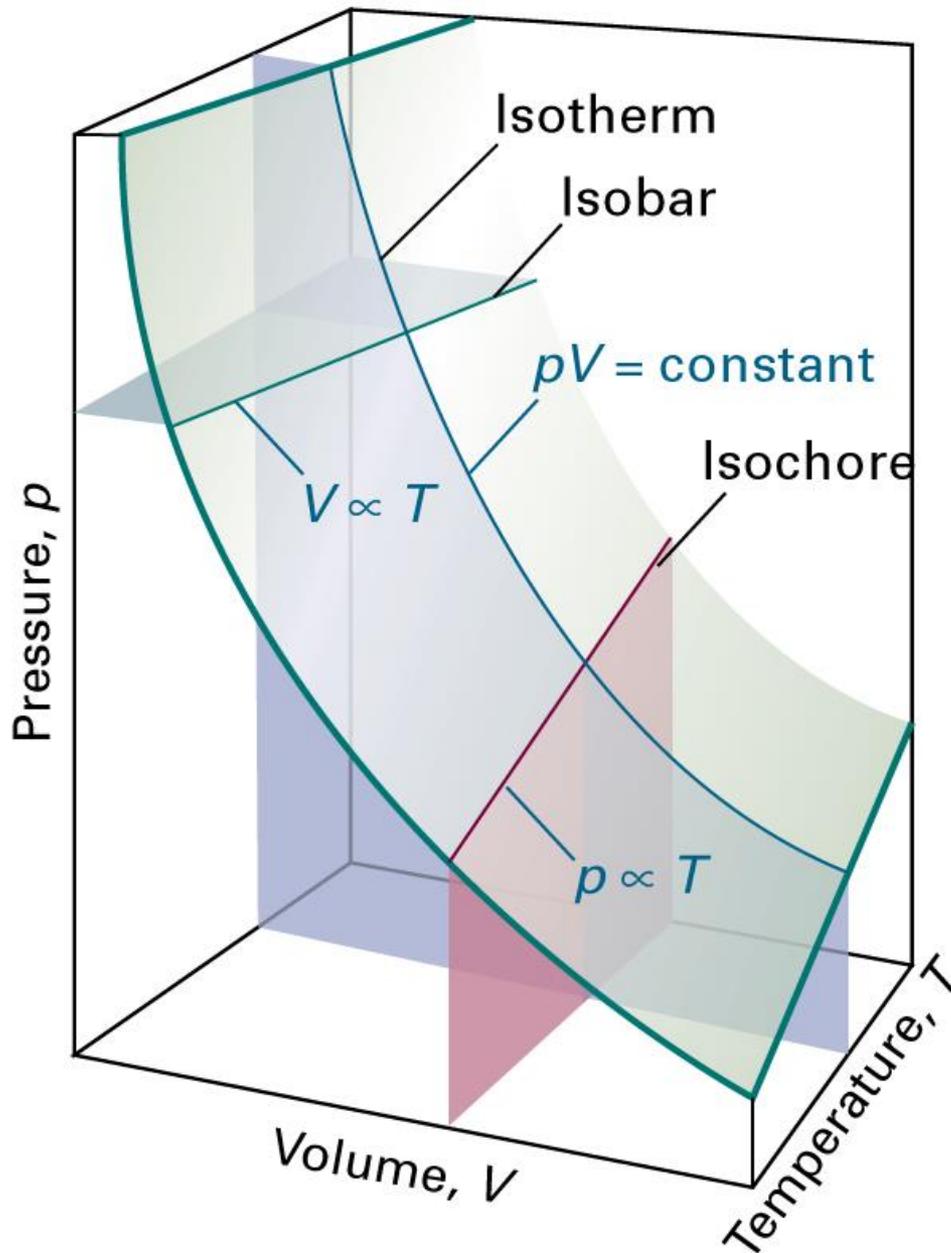
by Theoreticians



$$PV = nRT$$

Figure 1A.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.



$$PV = nRT$$

Figure 1A.7

Sections through the surface shown at a constant variable.

1B 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

$$z^{-1} = \tau : \text{Collision Time} \quad \text{Sec. 1B.2(a)}$$

The mean free path, λ : the average distance each particle travels between collisions

1B.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 $|2mv_x|$.

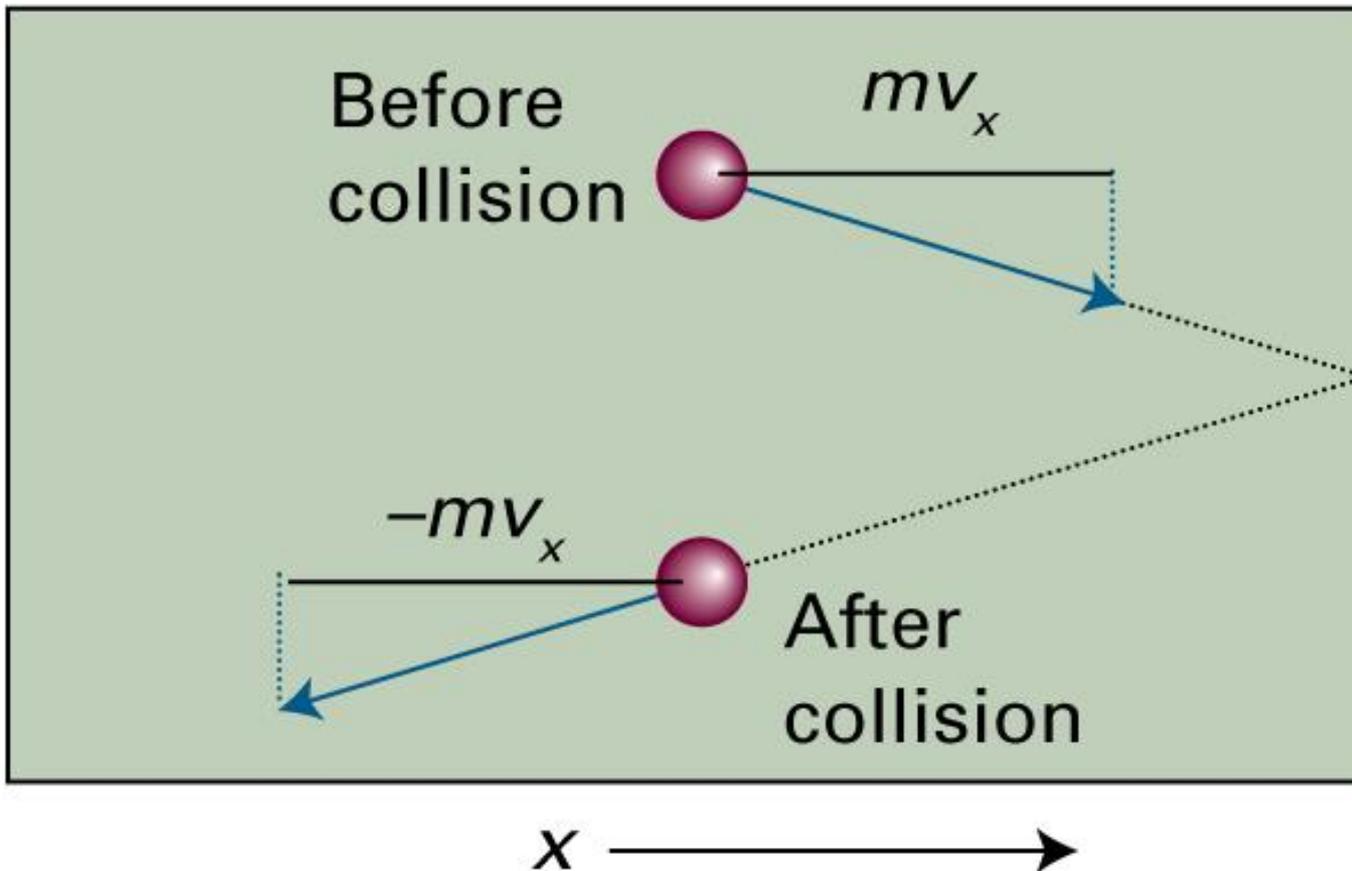


Figure 1B.1

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 Δt (IQ 1,000)

\approx

The number of molecules able to reach in that time

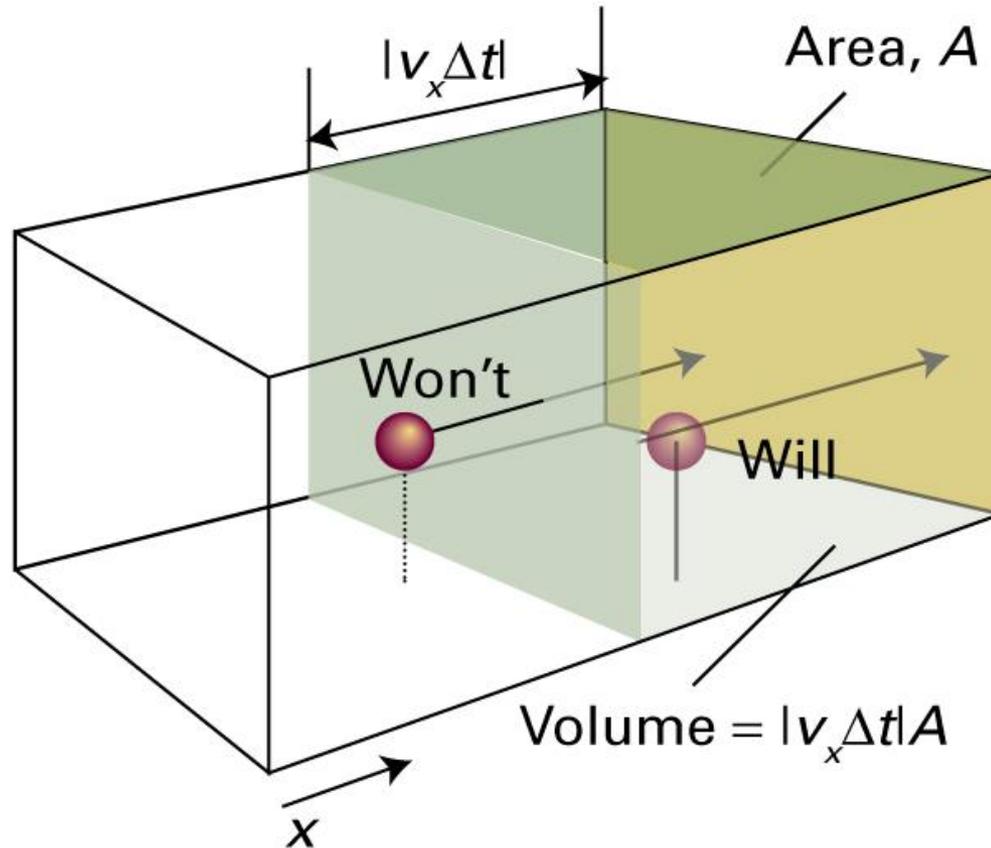


Figure 1B.2

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

The distance **a molecule of velocity v_x** can travel in a time $\Delta x = |v_x| \Delta t$, so all 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

$\frac{nN_A}{V}$: the **number of molecules** per unit volume

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

$\therefore \frac{nN_A A |v_x| \Delta t}{V}$: the number of molecules in the volume of interest

On the average, half of these are moving to the right, and half to the left, and so **the average number of collisions in the interval Δt** is $\frac{nN_A A |v_x| \Delta t}{2V}$

\therefore the total **momentum change**

$$= \frac{nN_A A v_x \Delta t}{2V} \times 2m v_x = \frac{nmN_A A v_x^2 \Delta t}{V} = \frac{nM A v_x^2 \Delta t}{V} \quad \text{where } M = mN_A$$

The rate of change of momentum = **force** = $\frac{nM A v_x^2}{V}$

The pressure = $\frac{nM v_x^2}{V}$

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,

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

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

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

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

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

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

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

증명 중

$$pV = nRT \\ = Nk_B T$$

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

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

root mean square speed of molecules

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1B.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 to $v_z + dv_z = f(v_x, v_y, v_z) dv_x dv_y dv_z$.

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

3-D

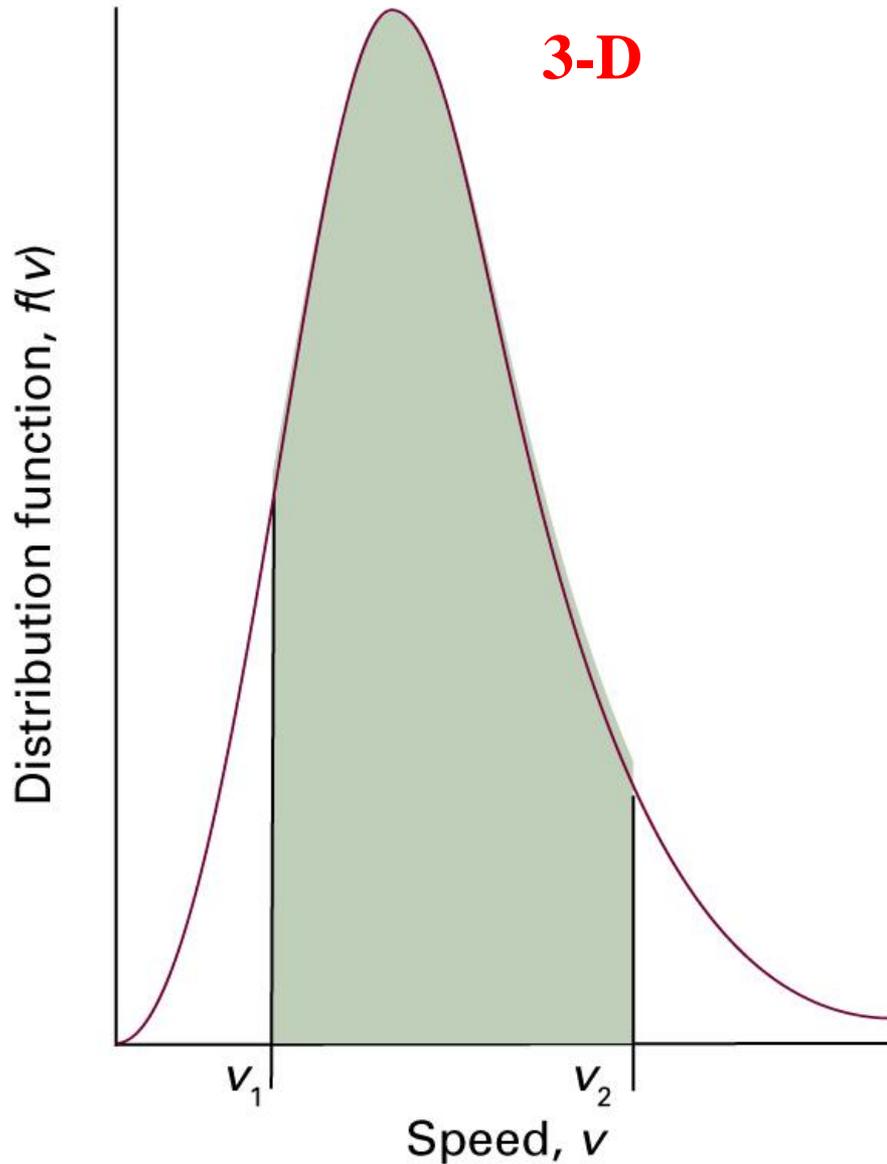


Figure 1B.6

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.

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

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

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

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

Why δv_x , not δE ?

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

1-D

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

Maxwell-Boltzmann distribution of molecular velocities **(1B.5)**

For three-dimensional case, the Maxwell-Boltzmann distribution

$$\begin{aligned} \underline{f(v_x, v_y, v_z)} dv_x dv_y dv_z &= \underline{f(v_x) f(v_y) f(v_z)} dv_x dv_y dv_z \\ &= \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} dv_x dv_y dv_z \end{aligned}$$

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

3-D

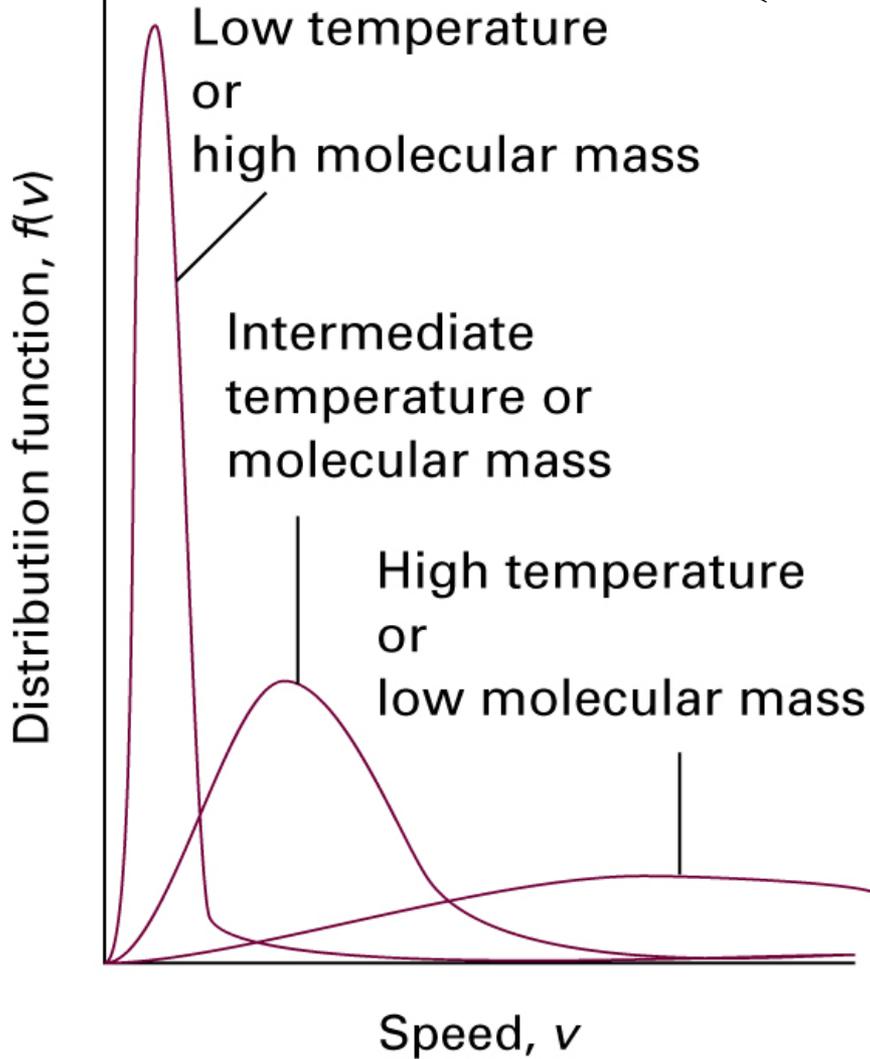


Figure 1B.4

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.

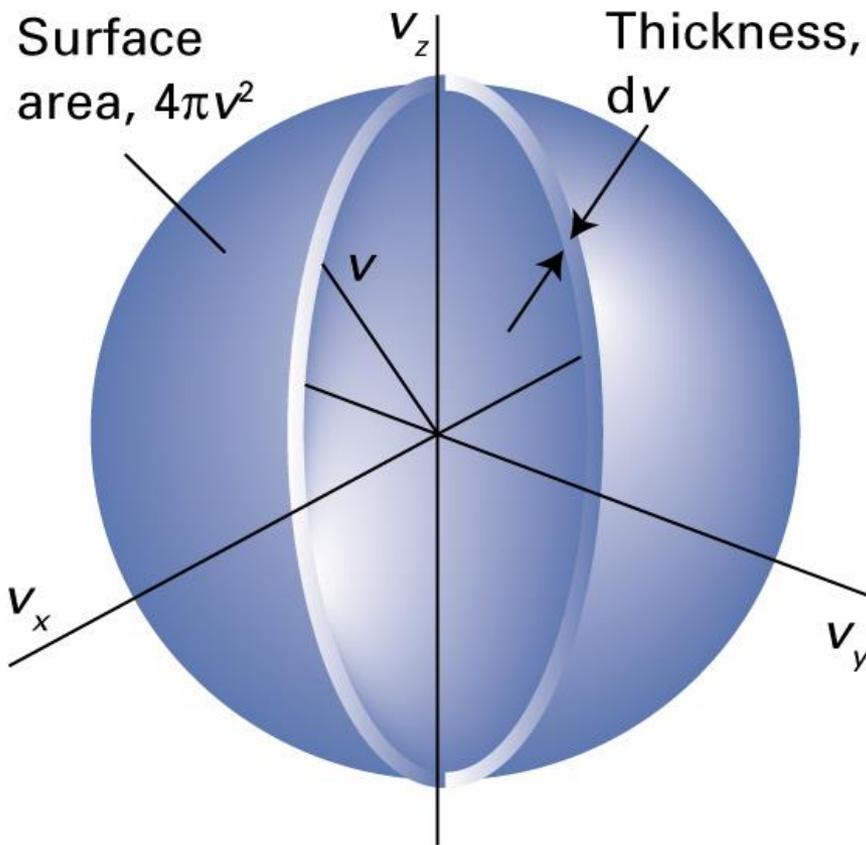


Figure 1B.3

The probability $f(v)dv$ that the molecule has a speed in the range v ($=\sqrt{v_x^2 + v_y^2 + v_z^2}$) 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 .

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:

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

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

3-D

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

1-D

Boltzmann Distribution

- (1) The root mean square speed is the square root of the average value of v^2 .

$$v_{rms} = \left(\frac{3RT}{M} \right)^{\frac{1}{2}} = \left(\frac{3kT}{m} \right)^{\frac{1}{2}} \quad (1B.7)$$

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

$$\langle v \rangle = \int_0^{\infty} v f(v) dv = \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}} \quad (1B.7)$$

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

$$v_{most\ probable} = \left(\frac{2RT}{M} \right)^{\frac{1}{2}} \quad (1B.9)$$

- (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 ,

$$v_{rel} = \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}}, \text{ where } \mu = \frac{m_A m_B}{m_A + m_B} \quad (1B.10a)$$

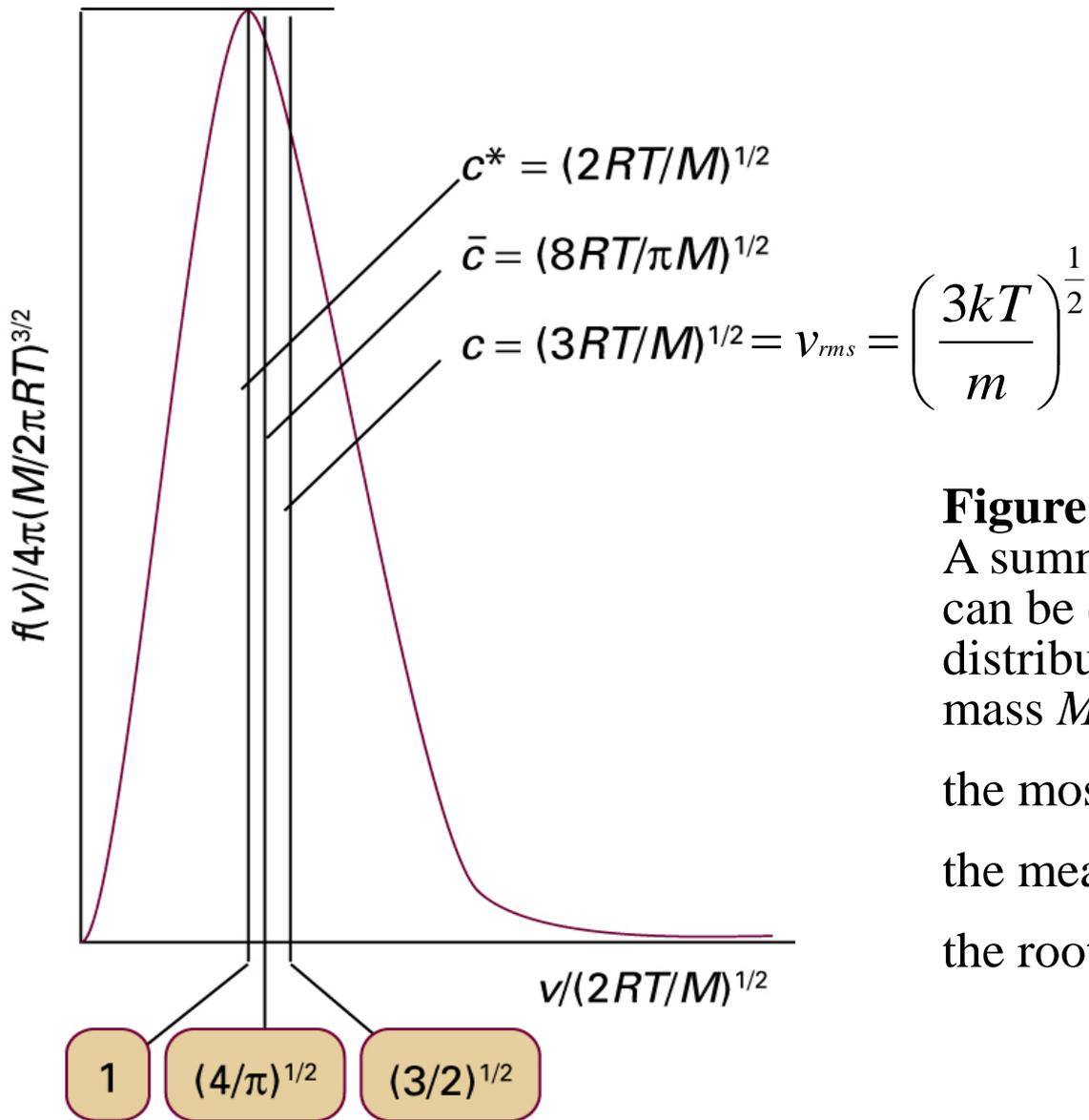


Figure 1B.7

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, and

the root mean square speed.

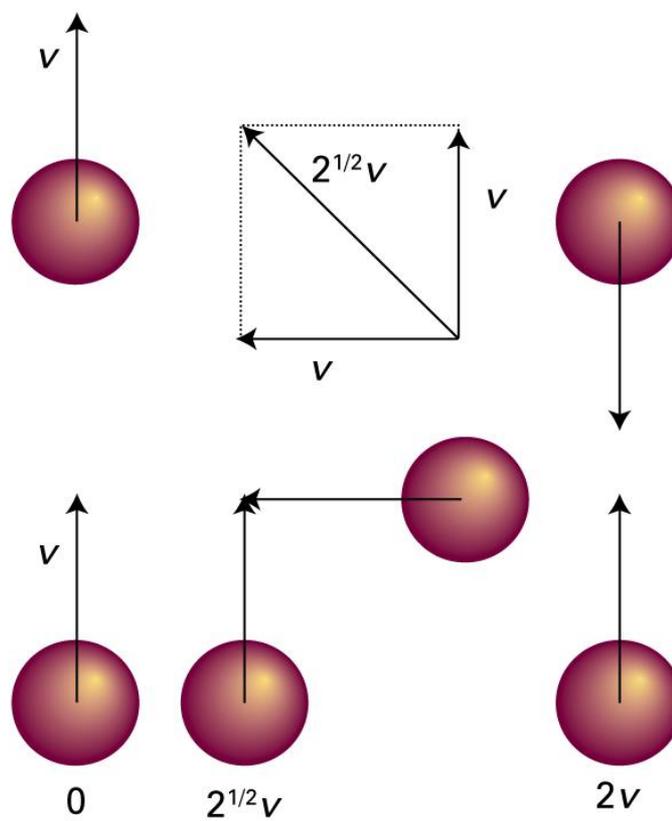


Figure 1B.8

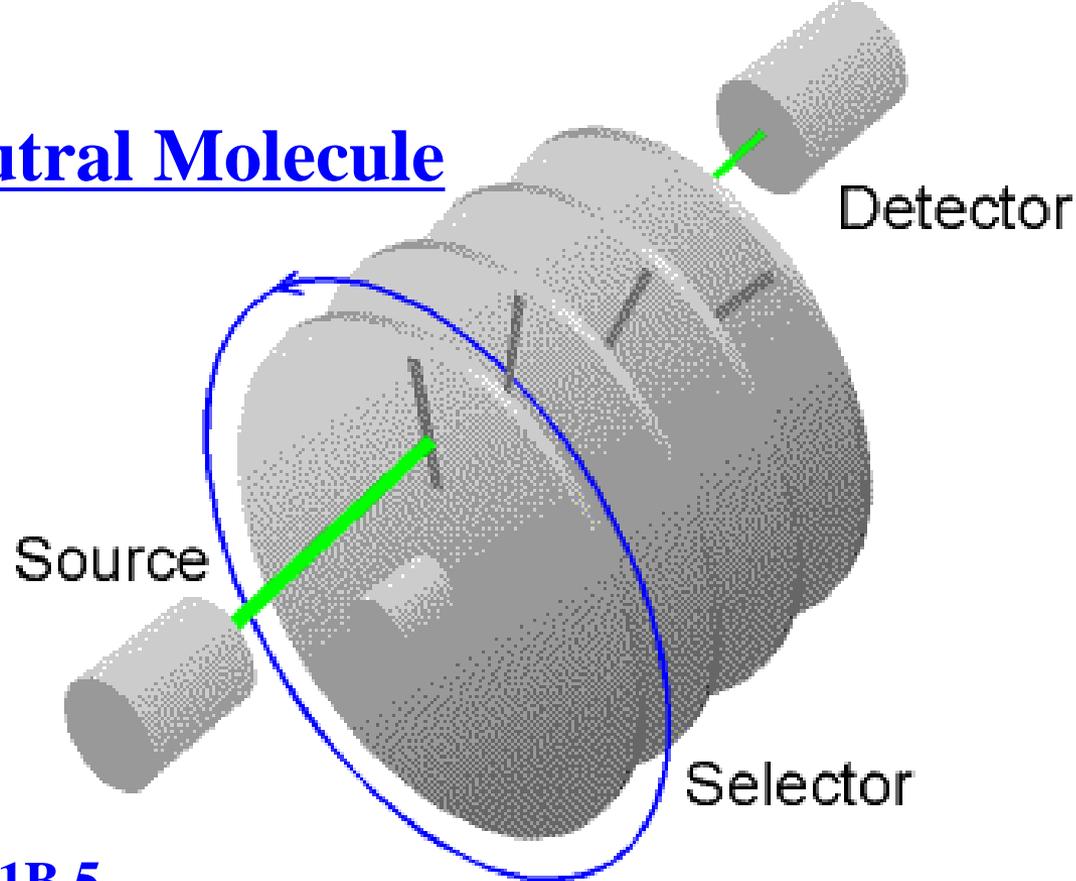
[A simplified version](#) of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed.

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

Neutral Molecule



Charged Molecule

charge/mass

through B

(magnetic field)

Fig. 1B.5

Velocity Selector = Time-of-Flight Measurement

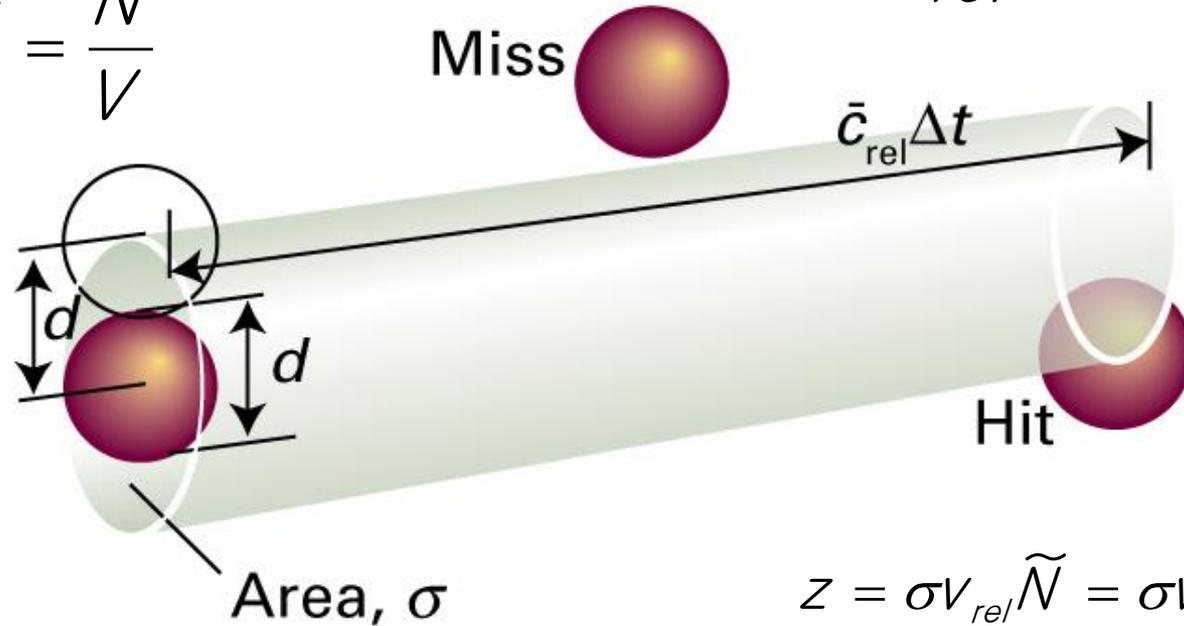
The molecules are produced in the source (which may be an oven with a small hole in one wall), and travel in a beam towards the rotating disks. Only if the speed of a molecule is such as to carry it through each slot that rotates into its path will it reach the detector. Thus, the number of slow molecules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

1B.2(a) $z^{-1} = \tau$: Collision Time

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

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

Cross Section



$$(1B.11a)$$

$$(1B.11b)$$

$$(1B.12)$$

$$(1B.13)$$

$$Z = \sigma v_{rel} \tilde{N} = \sigma v_{rel} \frac{N}{V} = \frac{\sigma v_{rel} \rho}{kT}$$

$$\text{Mean free path } \lambda = \frac{v_{rel}}{Z} = \frac{kT}{\sigma \rho}$$

Figure 1B.9

In an interval Δt , a molecule of diameter d 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 \sim mean speed

The mean free path λ ,

$$\lambda = \frac{\langle v_{rel} \rangle}{z} = \frac{1}{\sigma \left(\frac{N}{V} \right)} \quad z = \langle v_{rel} \rangle \sigma \left(\frac{N}{V} \right)$$

For a perfect gas,

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

The mean free path is inversely proportional to the pressure.

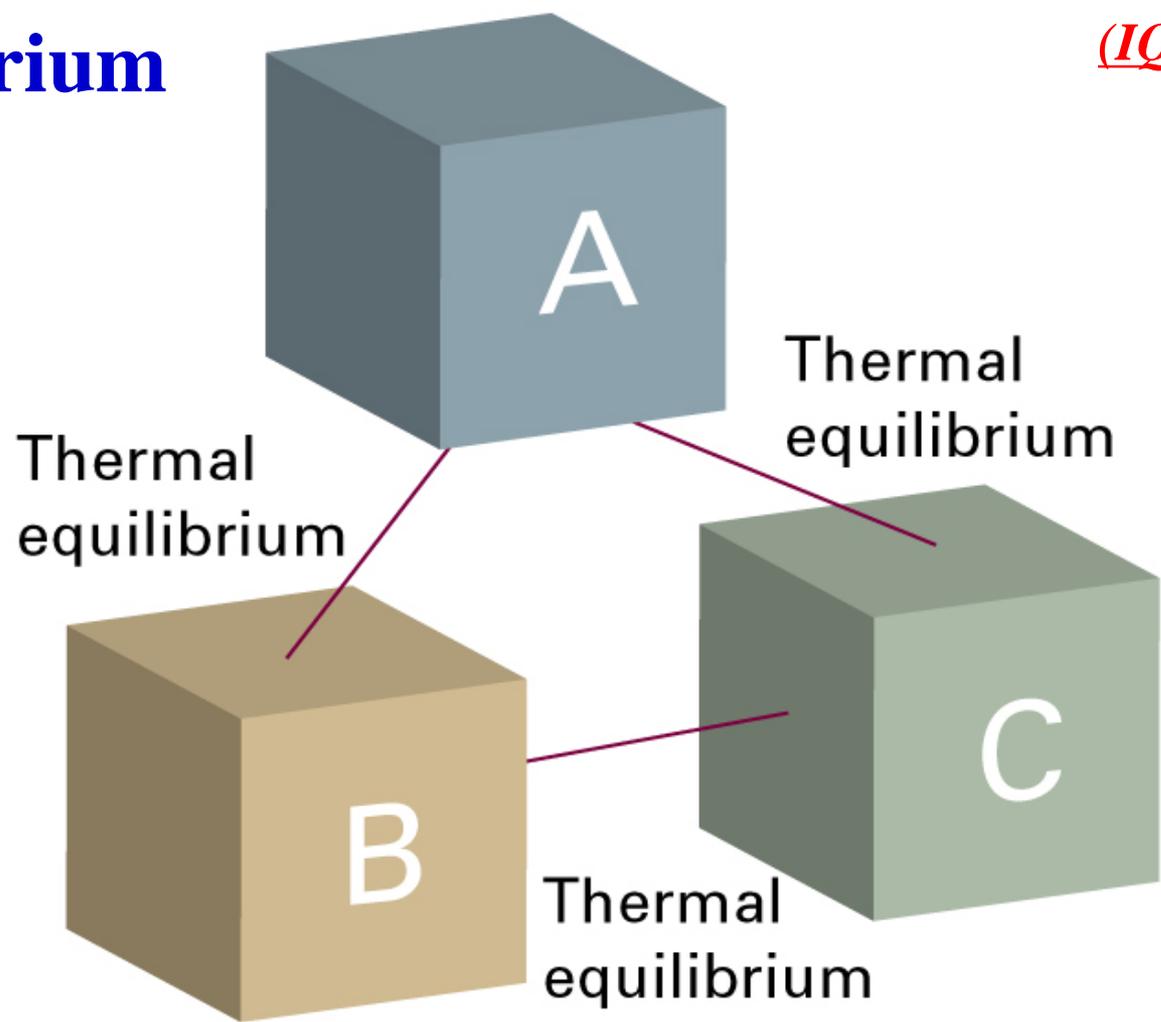
$$v = 500 \text{ m/s} \quad \tau = 1 \text{ ns} (= 0.5 \text{ ns})$$

$$v \tau = 300 \text{ nm} \quad \text{at } 300 \text{ K} + 1 \text{ atm}$$

$$10^{-5} \text{ atm} \sim 1 \text{ cm} \quad \text{at } 300 \text{ K}$$

Thermal Equilibrium

(IQ 50)



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.

1C Real Gases

1C.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.

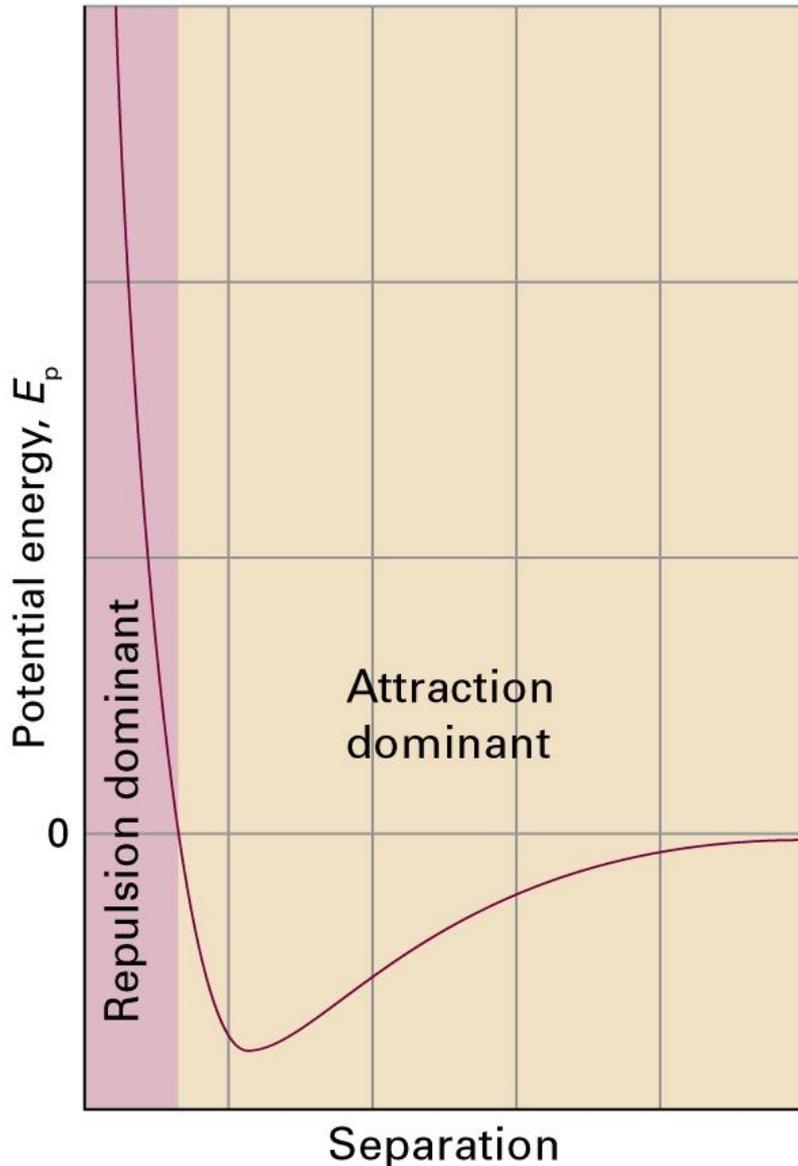


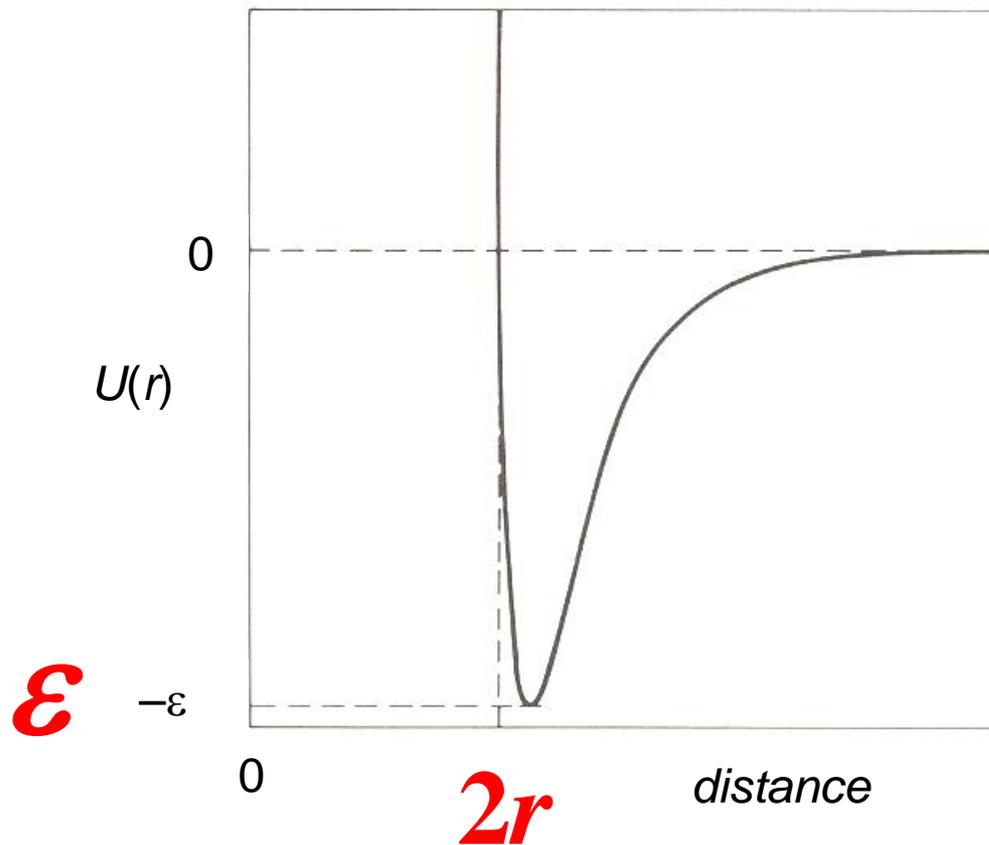
Figure 1C.1

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.

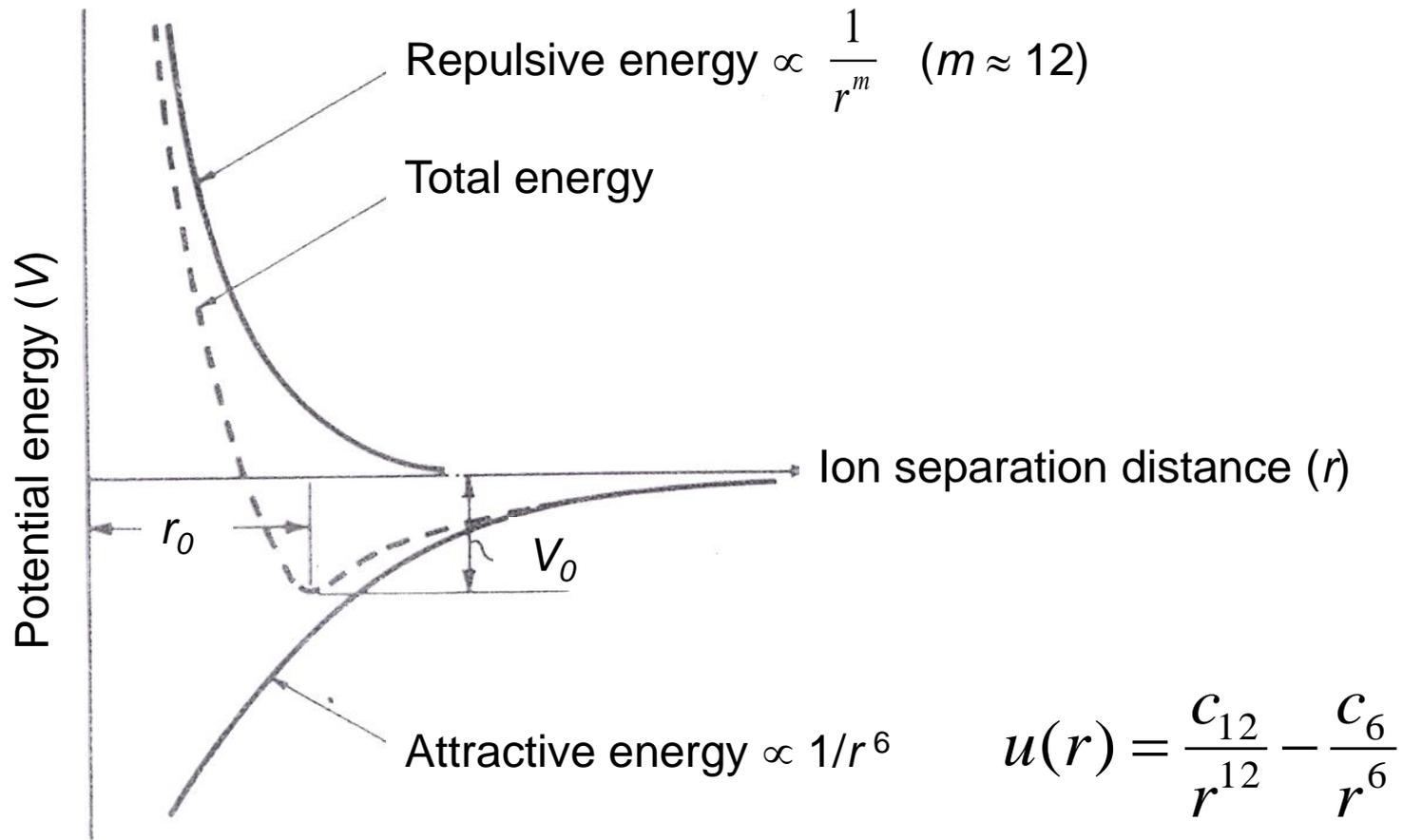
At intermediate separations, where the potential energy is negative, the attractive interactions dominate.

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



~Figure 1C.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 (ϵ), which is the depth of the potential well at its minimum.



~Fig. 1C.1

Energy vs. separation distance for two atoms (or two oppositely charged ions).

1C.2 The van der Waals Equation \cong *Real Gases*

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

$V_m = \text{molar volume}$

Ideal gas: 1. The size of molecule is negligible.
2. The interactions are negligible.

(1C.5b)

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

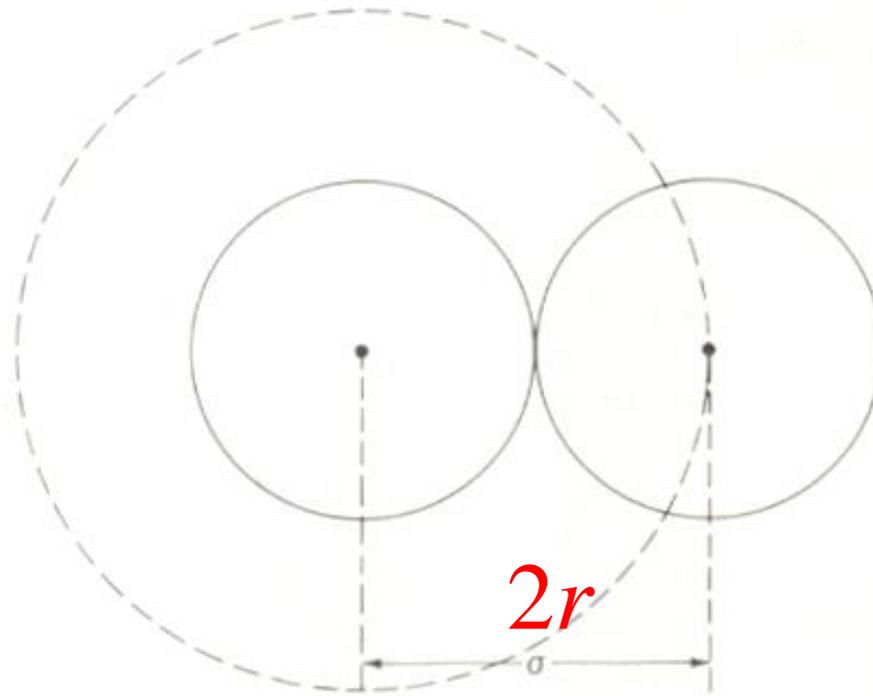
a \longrightarrow At finite concentrations, molecules will have **attractive forces** which will **reduce the pressure**.

b \longrightarrow 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.

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

[Justific. 1C.1]

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



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

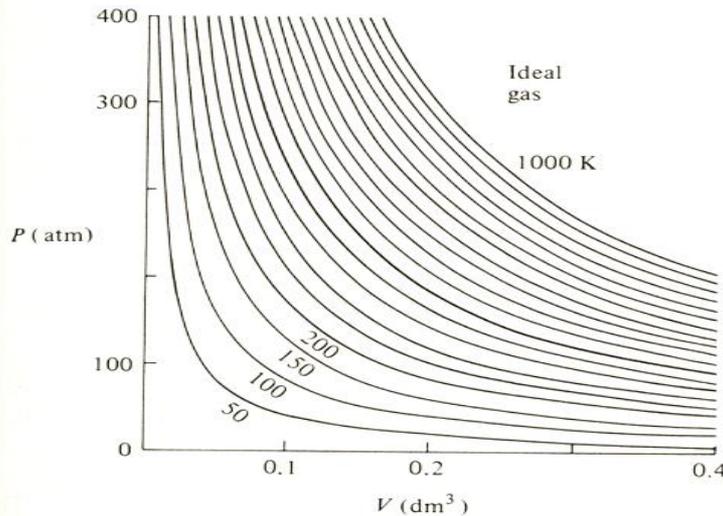
$P-V$ Dependence at Different Temperatures

Gas isotherms:

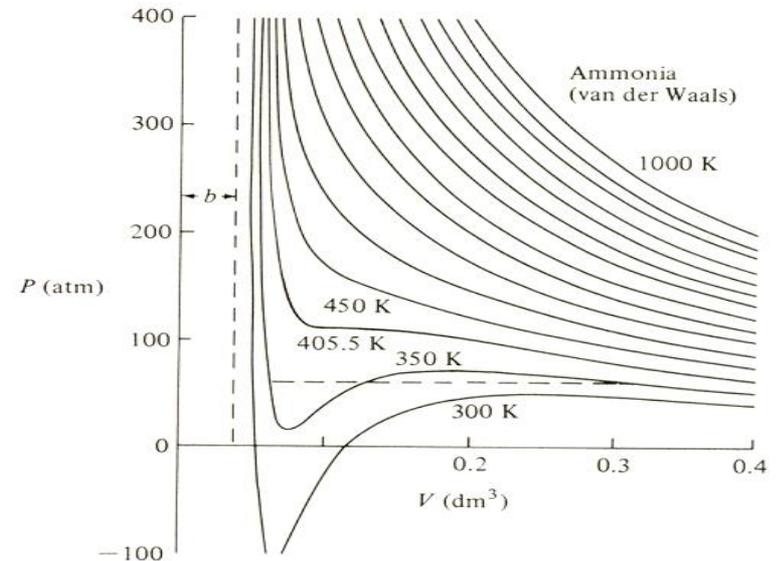
Comparison of the isotherms of an ideal gas to that predicted by the van der Waals equation for ammonia.

An ideal gas will not condense at any temperature.

Ideal Gas



Ammonia (van der Waals)



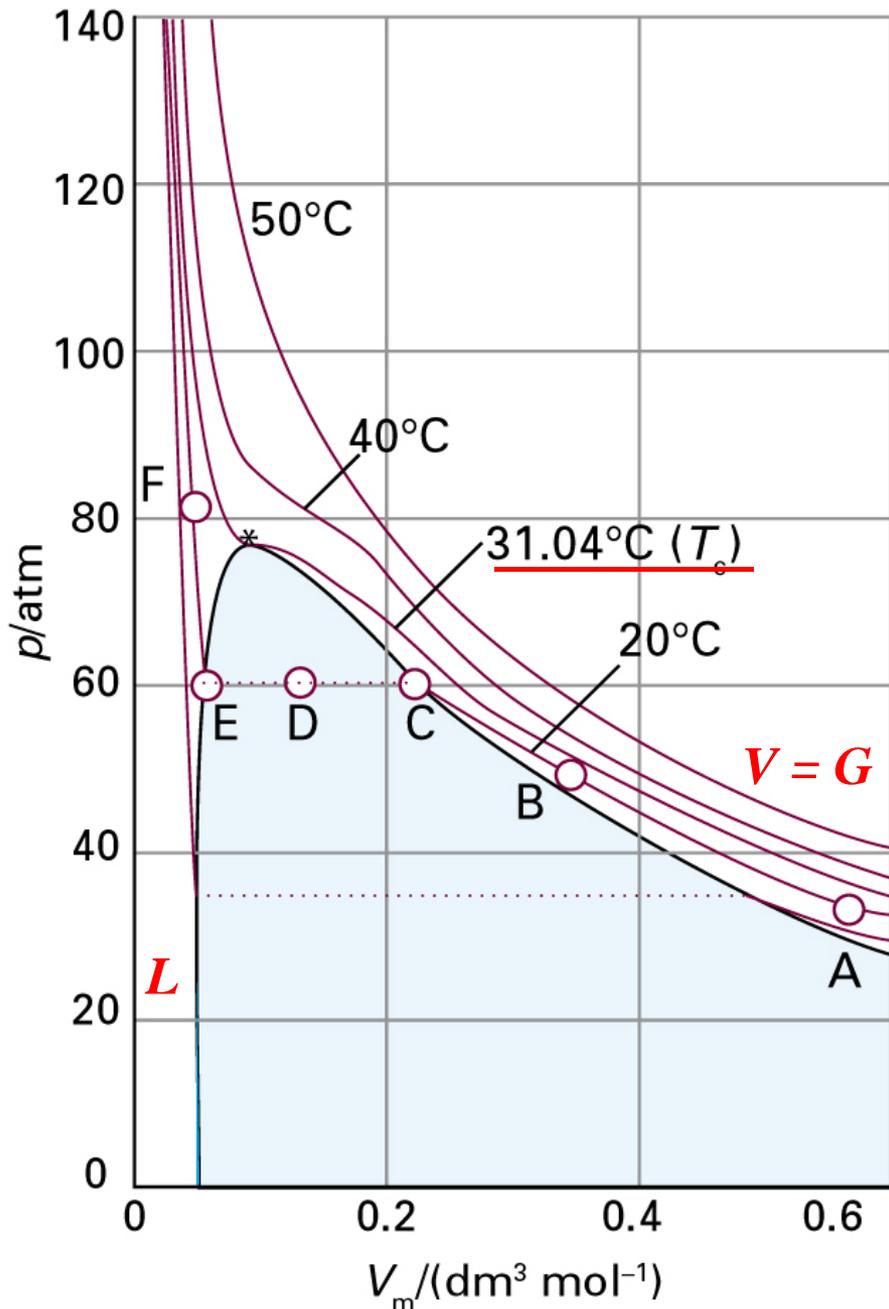


Figure 1C.2

Experimental isotherms of **carbon dioxide (CO_2)** at several temperatures.

The **critical isotherm ***, 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 & 31.04°C

Triple Point: 518 kPa & -56.6°C

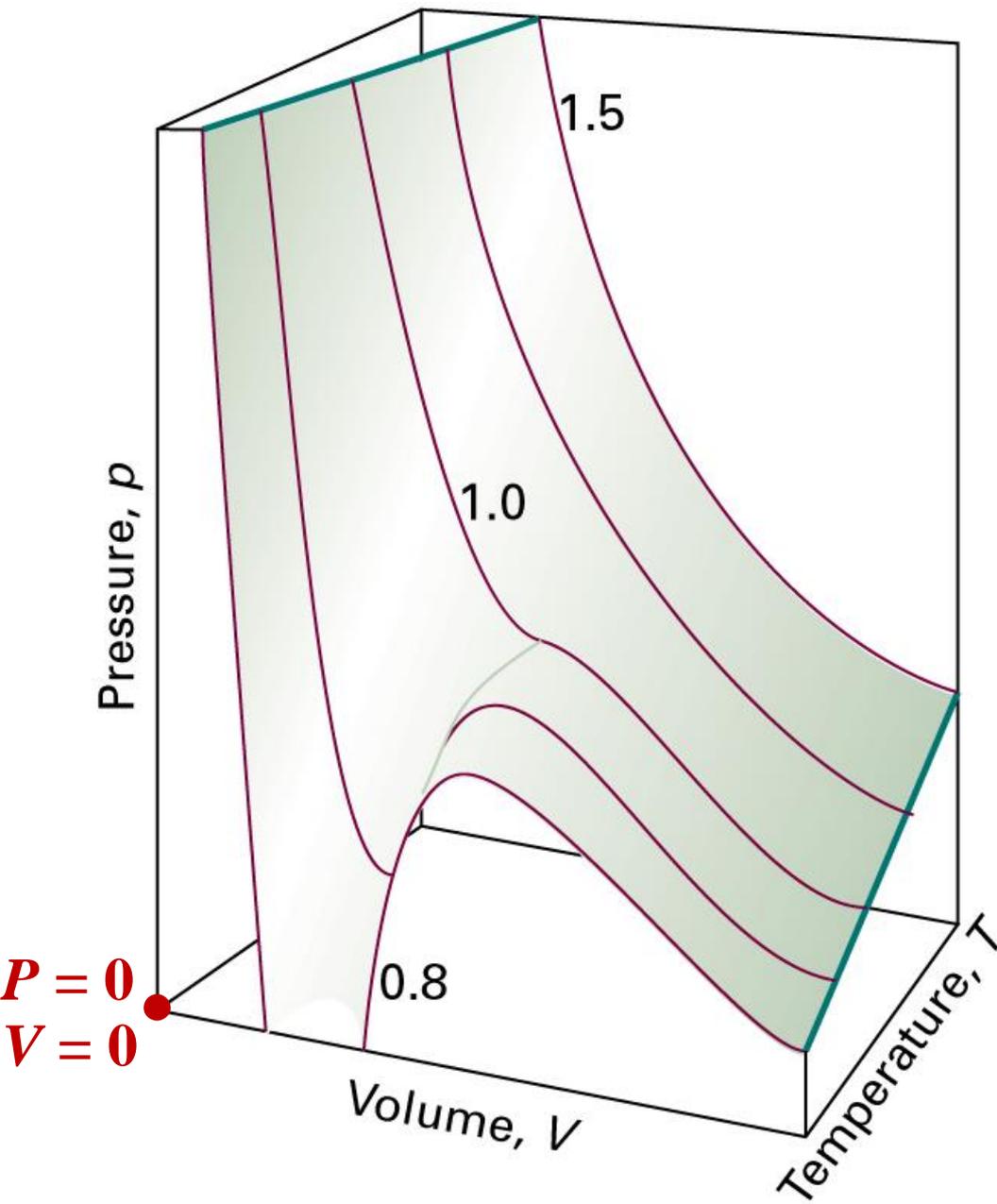


Figure 1C.7

The surface of possible states allowed by the **van der Waals** equation.

For van der Waals equation,

$T > T_c$, somewhat realistic

$T < T_c$, the isotherms show an **undulation** which is not at all like the observed behavior

Reason:

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 the white board)

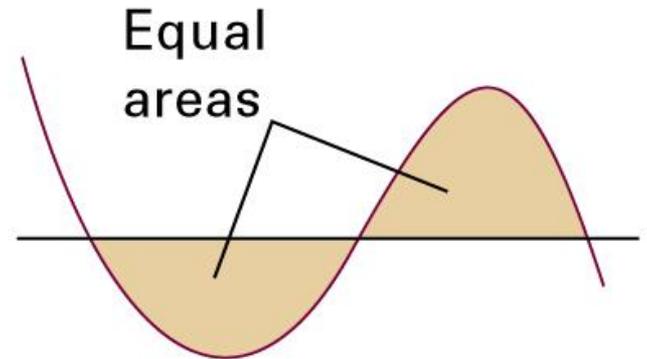
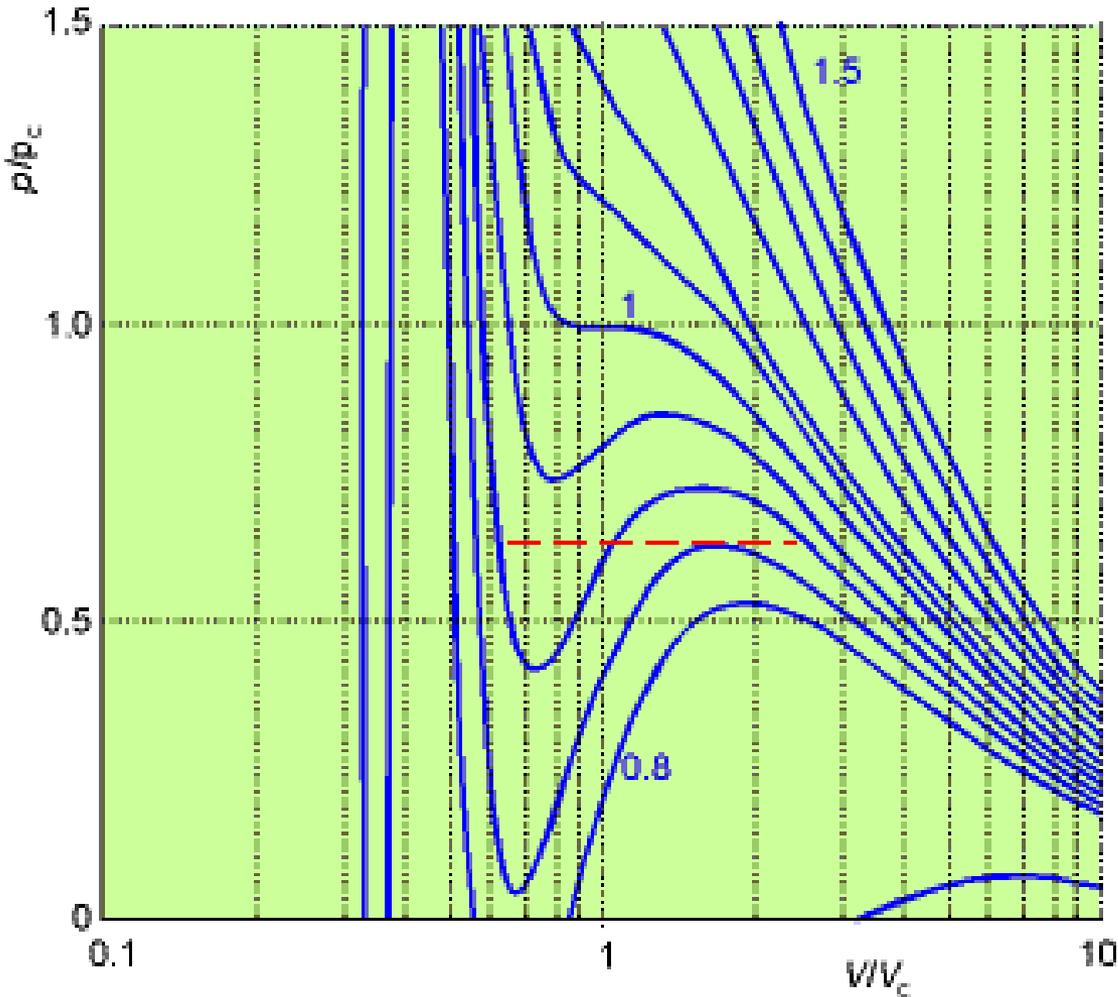


Figure 1C.7

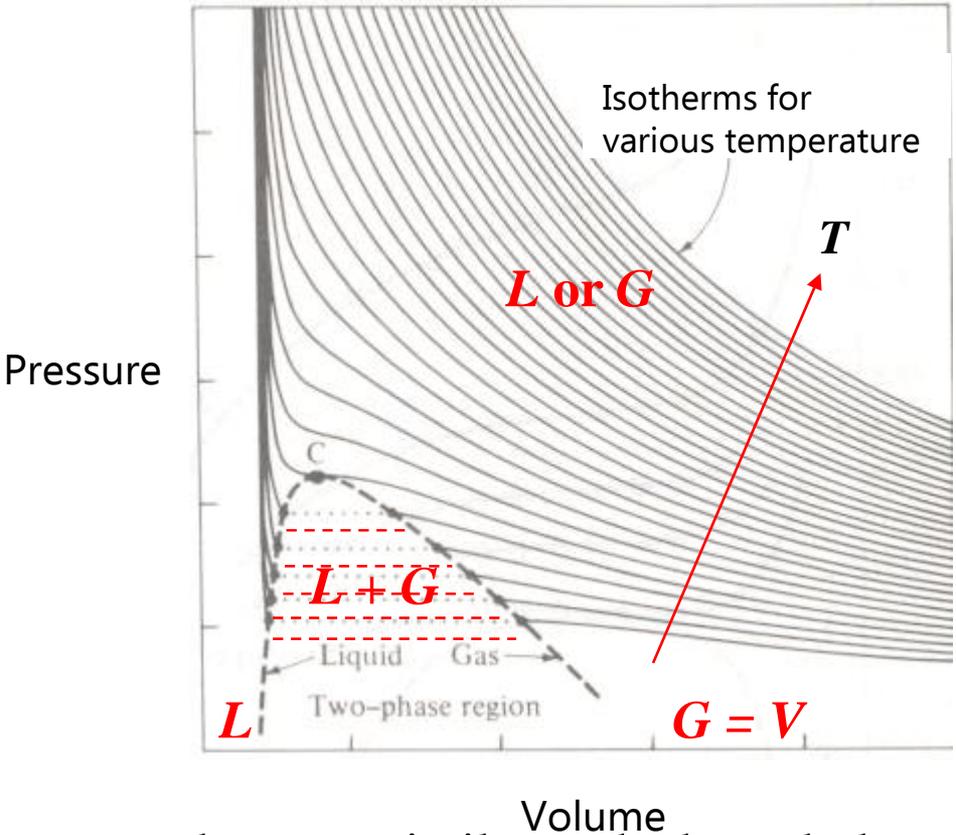
Van der Waals isotherms at several values of T/T_c .

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

The critical isotherm is the isotherm for $T/T_c = 1$.

Critical Behavior of Fluids

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



~Fig. 1C.7

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

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

Below the critical temperature, 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.

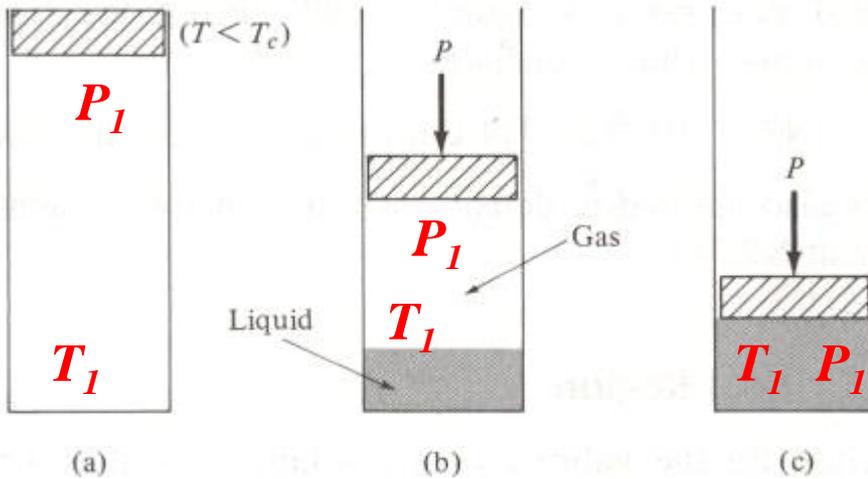
At the critical temperature, this becomes an inflection point for which the slope is zero at some point – namely, the critical point (P_c, V_c, T_c).

The meaning of the horizontal part of the isotherms below T_c :

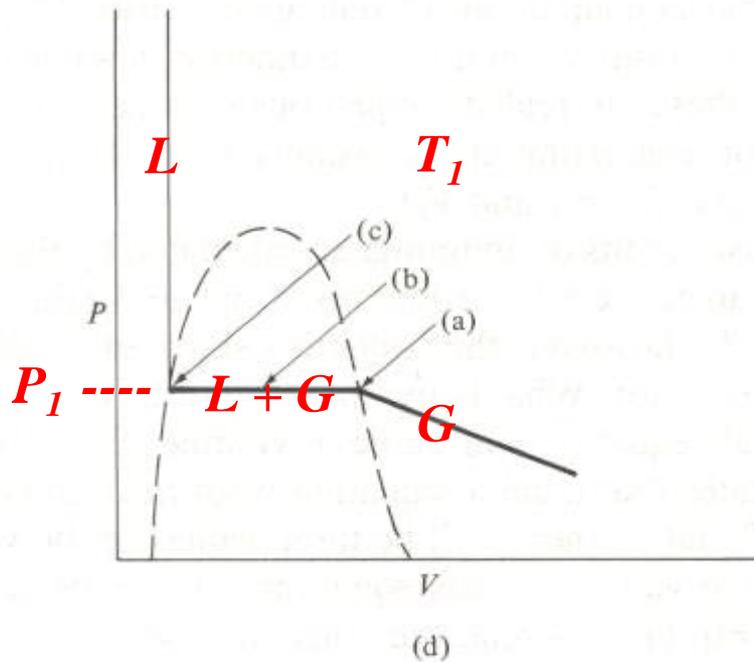
The value of the pressure at which, for a given temperature, liquid and vapor phases are in equilibrium (i.e., the horizontal lines) is called the vapor pressure.

The total volume of the fluid (liquid plus vapor) can be decreased without a change in pressure.

If there are two phases in the container, compression will cause more vapor to condense into the higher-density liquid, but at the same pressure.



at $T < T_c$



Liquefaction of a gas. The isothermal compression of a gas that is below its critical temperature will, at the pV point (a), cause the condensation of a liquid.

Further reduction of volume will cause more liquid to condense, but the pressure will not change; this is the

vapor pressure of liquid at this temperature.

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

1.4(b) Evaluation of Gas Constants from Critical Data

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

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

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

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

$$\left. \begin{array}{l} \frac{dp}{dV_m} = 0 \\ \frac{d^2p}{dV_m^2} = 0 \end{array} \right\} \text{ at } T = T_c, p = p_c, V_m = V_{m,c}$$

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

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

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

(1C.6)

Table (1C.4)

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

The gases He and CO₂ are very different in their behavior at any given temperature and pressures. However, if we compare them, each at its critical point, their compression factors are nearly the same.

$$\begin{array}{l} \text{He: } T_c=5.3 \text{ K, } \quad p_c=2.26 \text{ atm, } V_c=57.7 \text{ cm}^3/\text{mol} \quad \rightarrow \quad Z_c=0.300 \\ \text{CO}_2: T_c=304.2 \text{ K, } \quad p_c=73.0 \text{ atm, } V_c=95.6 \text{ cm}^3/\text{mol} \quad \rightarrow \quad Z_c=0.280 \end{array}$$

The law of corresponding states demonstrates that the compression factor (and many other intensive properties) of any gas can be

written as a **universal function** of the reduced variables:

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

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:

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

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

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

의미

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

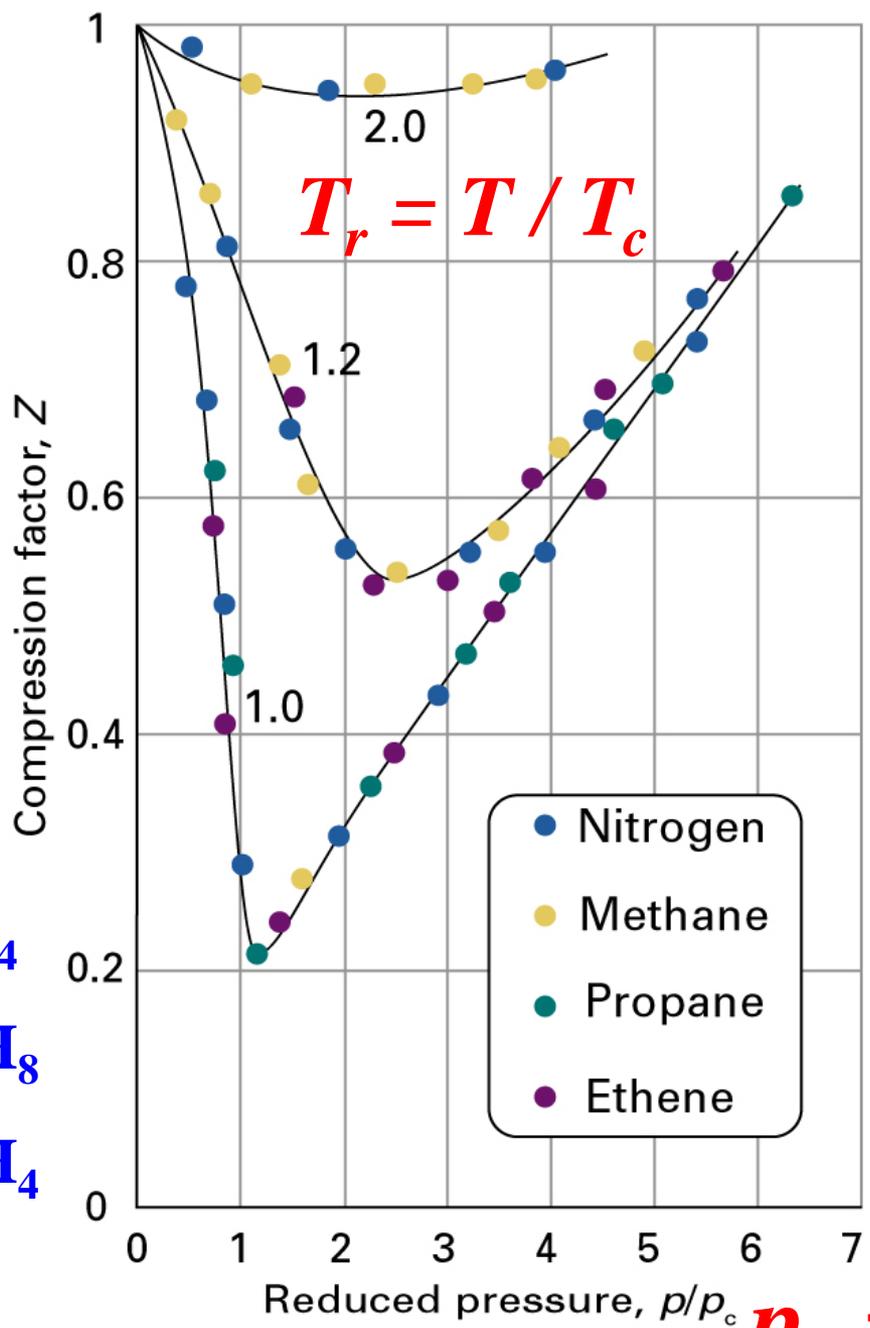
(1C.9)

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

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

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

N_2
 CH_4
 C_3H_8
 C_2H_4



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

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

Figure 1C.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 on to single curves.

$$p_r = p / p_c$$

1C.1(a) The Compression Factor

1C.1(b) The Virial Series

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

Define the compression factor:

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

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

For ideal gas, $Z \rightarrow 1$

(1C.2)

For real gas, $p \rightarrow 0, Z \rightarrow 1$

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

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

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

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

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

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

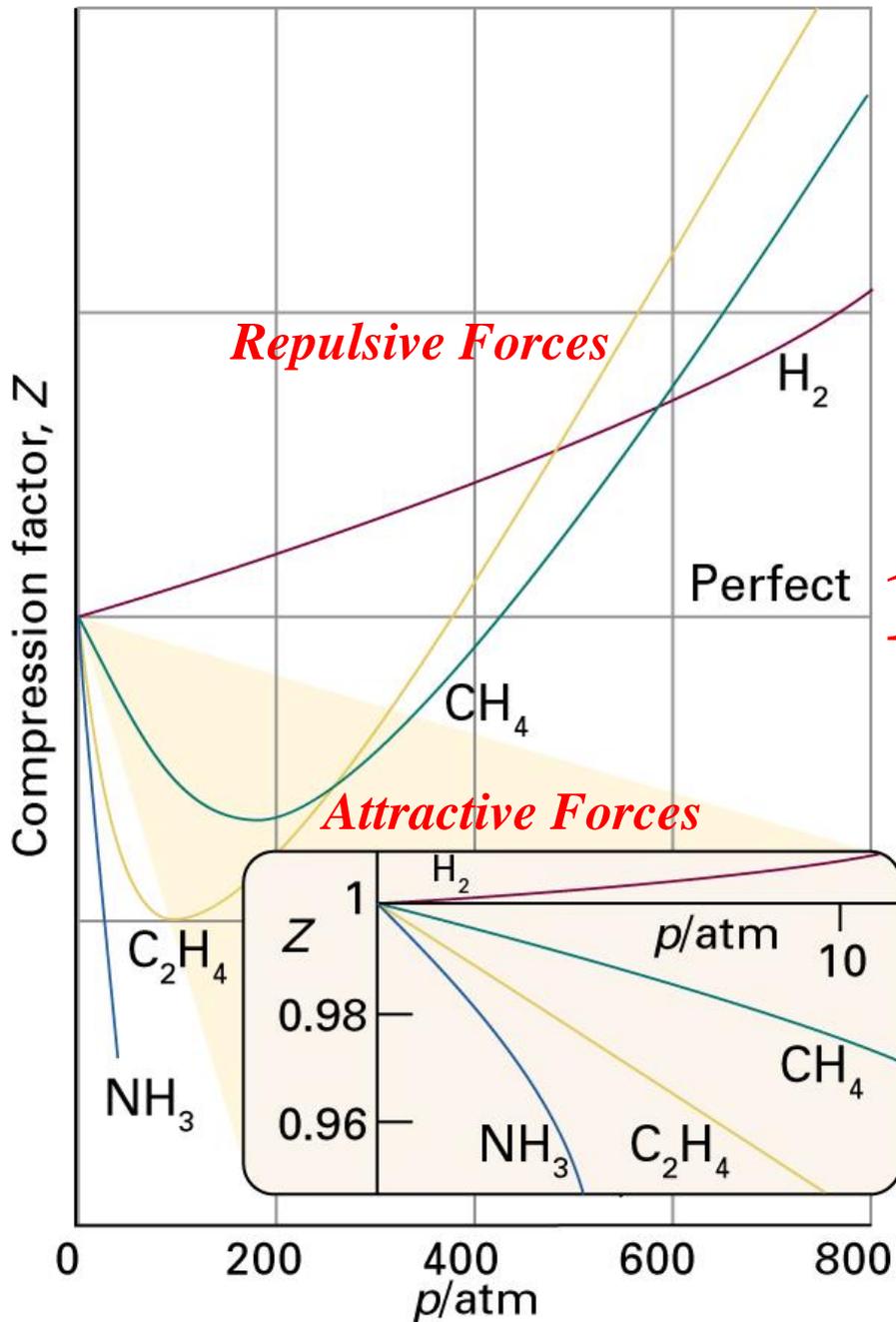


Figure 1C.3

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

Estimation of Virial Coefficients

The virial coefficients can be related to the [van der Waals constants](#).

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

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

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

$$\begin{aligned} Z(p, T) &= p V_m / R T \\ &= V_m / V_m^{ideal} \end{aligned}$$

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

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

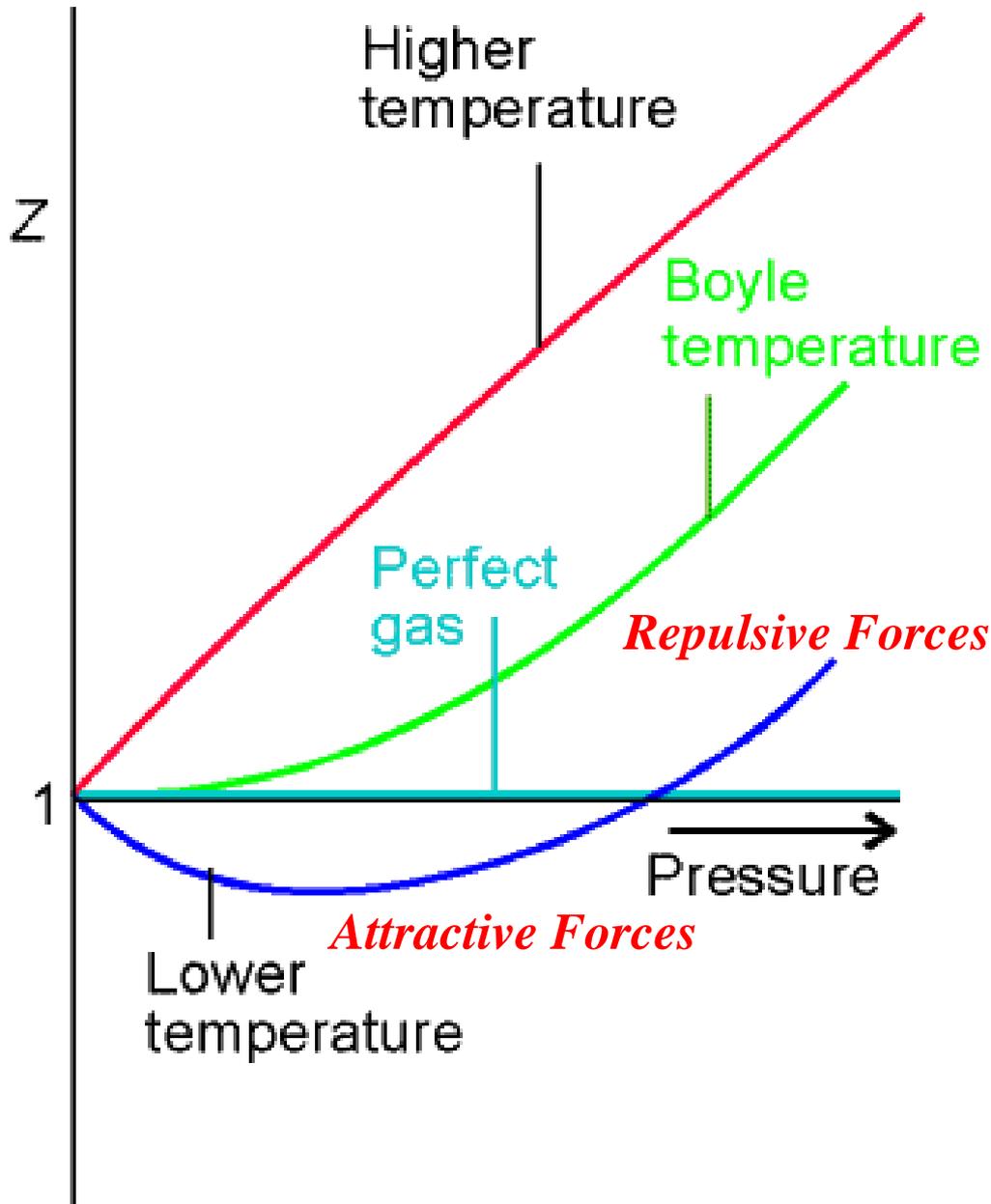


Figure 1C.4

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.

The Boyle Temperature

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

Boyle temperature \rightarrow the repulsive and attractive forces
cancel each other, giving nearly ideal behavior.

Example: Estimate the Boyle Temperature of N_2 :
the actual value is 324 K.

$$a(N_2) = 1.39 \text{ (dm}^6\text{atm/mol}^2\text{)}$$

$$b(N_2) = 0.0391 \text{ (dm}^3\text{/mol)}$$

Table 1C.3

From van der Waals constants,

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

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

The Lennard-Jones Potential

(See page 13)

Second virial coefficient

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

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

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

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

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:

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

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

Define a parameter

$$\tilde{B} = \frac{B}{b_0}, \quad \tilde{T} = \frac{T}{(\varepsilon/k)}$$
$$\tilde{B} = 3 \int_0^\infty \left\{ 1 - \exp \left[-\frac{4(\rho^{-12} - \rho^{-6})}{\tilde{T}} \right] \right\} \rho^2 d\rho$$

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 simplest assumption is that of an ideal mixture.

The ideal-mixing approximation assumes that the properties of a mixture are either the sum or the mean of the properties that the pure gases would have under the same conditions.

Dalton's law

$$p = \sum_i p_i \quad \text{where } \underline{p_i \text{ is the partial pressure}}, \text{ the pressure exerted by the individual gases.}$$

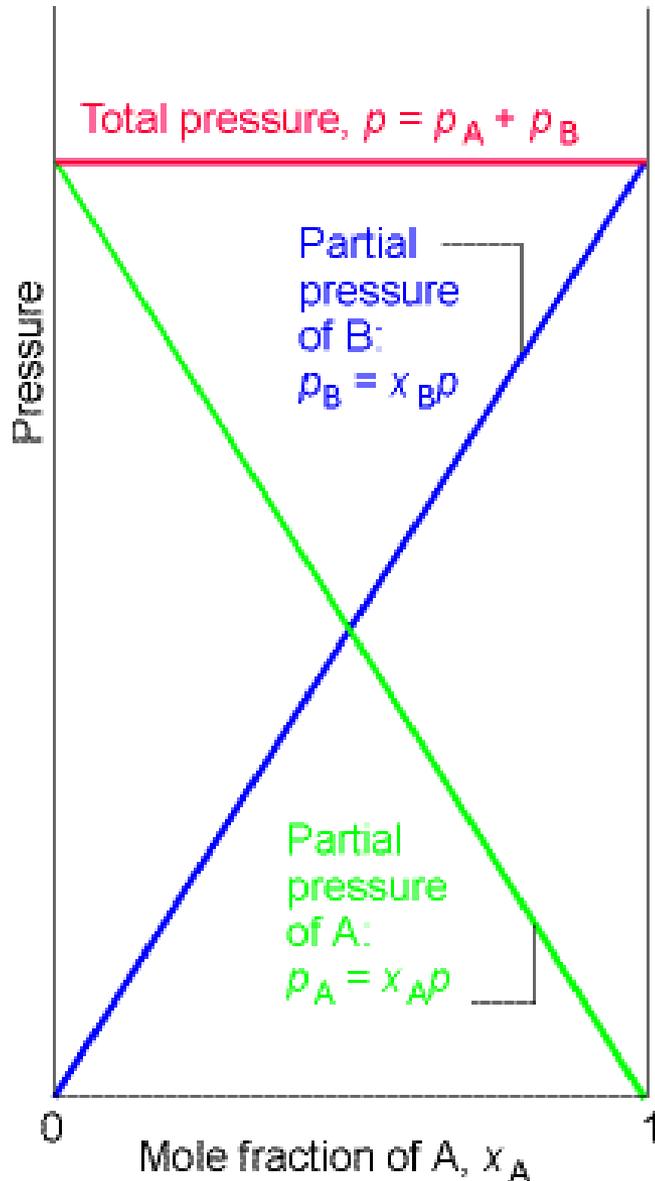
The total pressure of a gas is in proportion to the numbers of molecules present:

$$p_i = x_i p \quad \text{where } \underline{x_i \text{ is the mole fraction}}.$$

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

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

Ideal Mixture



$$P_i V = N_i k_B T$$

The partial pressures p_A and p_B of a binary mixture of (real or perfect) gases of total pressure p as the composition changes from pure A to pure B.

The sum of the partial pressures is equal to the total pressure.

If the gases are perfect (ideal), then the partial pressure is also the pressure that each gas would exert if it were present alone in the container.

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

1C.3(b) 1C.7(b)