Kinetic Theory of Gases

Prof.Dr. Shawky Mohamed Hassan

Theory of Gases

- Kinetic Theory of Gases
- Equations of Real Gases
- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases
- Properties of gases (Flash animation)

The Ideal Gas

CONTENTS

Common Properties

(A) gas expands to fill its container and its volume is readily contracts when pressure is applied.

(b) Two or more gases form homogeneous mixtures in all proportions, regardless of how different gases may be.

Equation of State

- To define properly the state or conditions, of a gas, it is necessary to assign values to certain variable quantities – namely,
- temperature (T), volume (V), pressure (P) and quantity (n).
- The state can be specified by giving the values of any three of these variables,
    - $F(n,V,P,T) = 0 \qquad (1.1)$

Equation of State

- Here F denotes some relationship between the variables.
- Particular forms of equations like Eq. (1.1) are called equations of state. They can be obtained by;

(1)Fitting experimental n, V, P,T data to empirical equations.

- Examples of these empirical equations are the followings:

Equation of State

- Law of Boyle PV = const. at const. T
- Law of Charles V/T = const. at const. P
- Law of Amontons P/T = const. at const. V
- Combined law PV/T = Const. n
- Principle of Avogadro V/n = const . at n and P

(2) **Theoretical equations** can be derived from models of gases such as that proposed by the kinetic theory of gases.

The Ideal-Gas Equation of State

- An ideal gas is defined as a gas that has the following equation of state:

$$PV = nRT \qquad (1.2)$$

- Here R is a universal gas constant. Its units depend on that used for P and V, since n and T have usually the units models (mol) and degree Kelvin (K).

Note: $R = PV / nT = \text{work} / nT = \text{Energy} / \text{Mol} \times \text{Kelvin}$

The Ideal-Gas Equation of State

*A standard condition of temperature and pressure (**STP**)*

- ***T*** *= 273.15 K*

- **P** *= 101.32 k Pa (1 atm)*

Using Eq.1.2 we have that;

- $\overline{V}$ *(The volume of one mol)* = 0.022415 m^3 **at STP**

Exercise

Determine the different values of R using Eq. 1.2.

THE MOLECULAR KINETIC THEORY OF GASES

- The properties of a prefect ideal gas can be rationalized qualitatively in terms of a model in which the molecules of the gas are in continuous chaotic motion.
- We shall now see how this model can be expressed quantitatively in terms of the kinetic theory of gases.

Assumptions of the Theory

- Gases consist of discrete particles called molecules which are of a negligible volume in comparison with that of the container.
- The molecules are in continuous random (caotic, Brownian) motion independent of each other (do not repel or attract each other) and travel only in straight lines between brief perfectly elastic collisions (no change in kinetic energy).

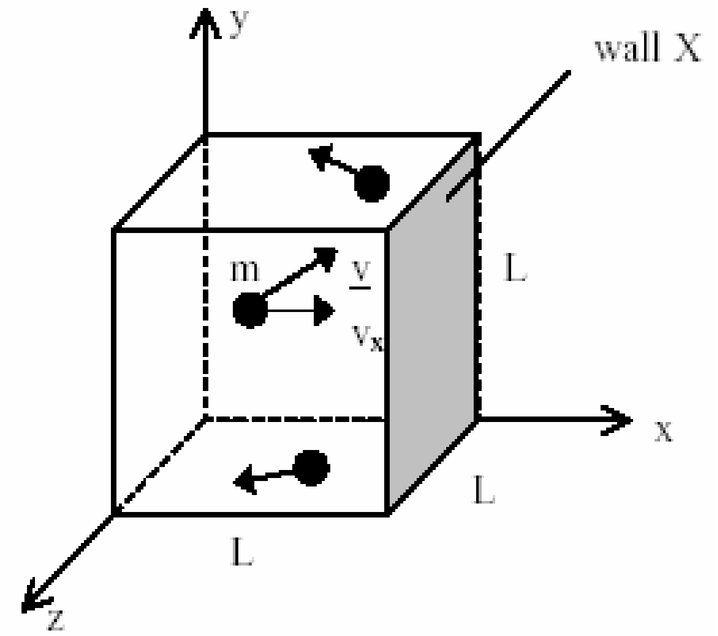
Assumptions of the Theory

- The pressure of the gas is due to the collisions of molecules.
- The kinetic energy due to the transitional motion of a mol of gas molecules is equal to (3/2) RT.

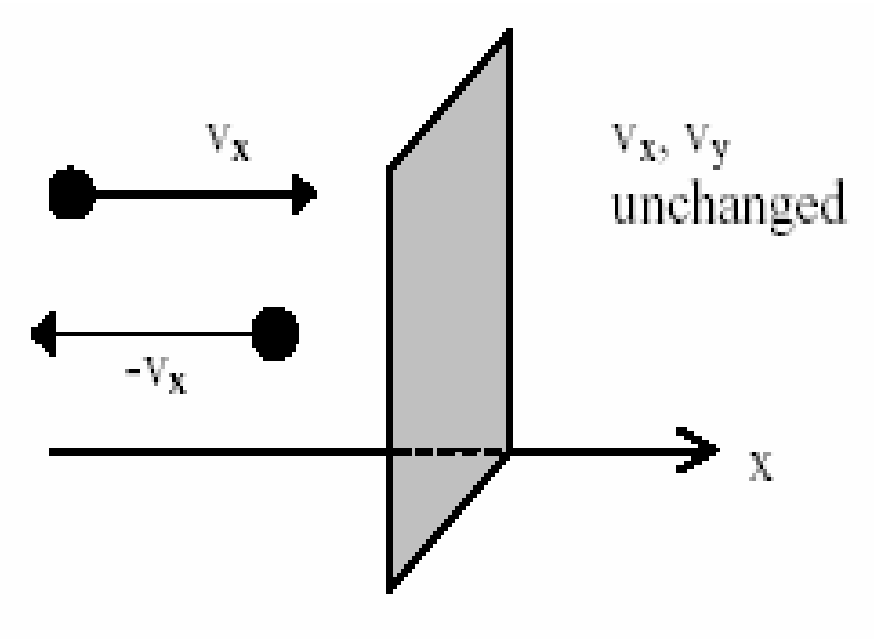
Pressure of the Gas

- Consider N molecules of an ideal gas, in a cubic container of side L (m).
- A typical molecule has mass m (kg), and velocity u (u_x, u_y, u_z) (ms^{-1})

Pressure of the Gas



Click Here to see flash file



Click Here to see flash file

We can calculate the gas pressure as follows

1.The pressure (P) is defined as the force (F) per unit area (A), viz.

$$\boxed{P = \frac{F}{A}} \qquad (1.3)$$

2.The force exerted by gas molecule is defined as the rate of change of momentum, that is

$$\boxed{F = \frac{\Delta(mu_x)}{\Delta t}} \qquad (1.4)$$

We can calculate the gas pressure as follows

3. For one molecule in x direction, the momentum is $mu_{\mathbf{x}}$, and change of momentum per collision = $mu_x - (-mu_x)$

$$= 2\,mu_x \qquad (1.5)$$

4. Rate of change of momentum per molecule

per collision= change of momentum x number of collisions per second

We can calculate the gas pressure as follows:

- The number of collisions per second $= \dfrac{u_x}{2L}$ (1.6)

From Eqs. (1.1) – (1.5) we can find that the pressure on the wall A as

$$P_x = \frac{mu_x^2}{V^3} \qquad (1.7)$$

where V = L^3 is the volume of the container.

- Now we can recognize that the pressure is the same for all walls of the container. Thus we can discard the restriction “by side A”. We therefore have

$$P = \frac{mu_x^2}{V^1} \qquad (1.8)$$

We can calculate the gas pressure as follows

- Now consider N molecules, instead of just one, the net pressure becomes as

$$P = \frac{N(mu_x^2)_{av}}{V} \qquad (1.8)$$

We can calculate the gas pressure as follows

If $\overline{Nmu_x^2}$ is written to indicate an average value, we have

$$P = \frac{\overline{Nmu_x^2}}{V} \qquad (1.9)$$

A relation between the pressure and the speeds of the molecules, rather than a component of the speeds, is more convenient.

- The velocity vector can be resolved into three orthogonal components to give

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

We can calculate the gas pressure as follows

- For a large number of molecules moving in random directions

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \text{ and } \overline{u^2} = \overline{3u_x^2} \qquad (1.10)$$

Substitution of Eq. (1.10) in Eq. (1.9) gives the desired relation between P and V

$$P = \frac{\frac{1}{3}\overline{Nmu^2}}{V} \quad \textbf{or} \quad PV = \frac{1}{3}\overline{Nmu^2} \qquad (1.11)$$

We can calculate the gas pressure as follows

- This important equation is as far as one can go to explain the basis for the pressure of a gas from the four kinetic-molecular postulates set out earlier.
- An additional postulate must be added to reach a result that can be compared with the empirical ideal-gas laws.

$$F = N\frac{\Delta(mu)}{\Delta dt} = N\frac{2mu}{1s}$$

$$\frac{(6.02x10^{23})(2)(32x10^{-3}\,kg\ mol^{-1})(500ms^{-1})/(6.02x10^{23}))}{1s}$$

Example 1.1

1 mol of O_2 molecules is confined in a container and struck each of its walls each second. Calculate

(a) the total force that the molecules exert on the wall if their speed is 500 ms^{-1}?and

(b) the pressure of the gas if the area of each wall is 20 cm^2 and

(c) u_{rms} (root mean square speed) .

Solution

(a) According to Eq. (1.3) and (1.4) the force exerted by one molecule is related to the rate of change of momentum. In 1s, the force exerted by N molecule is

Example 1.1

$$F = N\frac{\Delta(mu)}{\Delta t} = N\frac{2mu}{1s}$$

$$\therefore F = \frac{(1x10^{23})(2)(28x10^{-3}\,kg\ \mathrm{mol^{-1}})(6.022x10^{23}\ \mathrm{mol^{-1}})(450\ \mathrm{m.s^{-1}})}{1s}$$

= 4.2 kg.m.s^{-2} = 4.2 N

The corresponding pressure is

$$P = \frac{f}{A} = \frac{4.2\ \mathrm{N}}{(10\mathrm{cm}^2)(10^{-2}\,m/1\,\mathrm{cm})^2} = 4200\mathrm{N\,m^{-2}}$$

= 4200 Pa

Example 1.3

Calculate the transnational kinetic energy E_k of 1 mol of gas molecules and $\in_k$ for 1 molecule at 25°C.

Using in Eq.(1.11) and that $N = nN_A$, $E_k = ½\, mu^{-2}$, and $PV = nRT$,

∴

we have

$$PV = nRT = \frac{2}{3}(nN_A)\left(\frac{\overline{mu^{-2}}}{2}\right)$$

∵ $E_k = 3/2\ RT$ (1.12)

$E_k = 3/2(8.314\ \text{JK}^{-1}\ \text{mo}^{l-1})\ (298\ \text{K}) = 3.718\ \text{kJ mol}^{-1}$

Example 1.3

For 1 molecule

$$\in_k = \frac{3}{2}\frac{R}{N_A}R = \frac{3}{2}kt \qquad (1.13)$$

where k is the Boltzmann constant

$\in_k$ =3/2(1.3806x10^{-23} JK-1)(298 K) = 6.174x10^{-23} J

Quiz 1

1.1 What do you understand by the terms?

(a) Chaotic motion (b) Elastic collision

(c) Ideal gas (d) Empirical Formula

1.2 State the following laws in words;

(a) T – V law, (b) T – P law,

(c) P – V law, (d) PVT law and

(e) P – n Principle.

1.3 What model of a gas was proposed by the kinetic theory of gases.

Quiz 1

1.4 How are the following related?

(a) Torr and atm,

(b) Pascal and atm,

(c) Force and pressure,

(d) Pascal and joule,

(e) Gas const. and work ,and

(f) Kinetic energy and temperature.

1.5 Explain in terms of the kinetic theory of gases;

(a)Why two, given the freedom to mix, will always mix entirely?

(b) How heating makes a gas expand at constant pressure?.

(c) How heating a confined gas makes its pressure increase?

Theory of Gases

- Kinetic Theory of Gases
- Equations of Real Gases
- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases

Equations of Real Gases

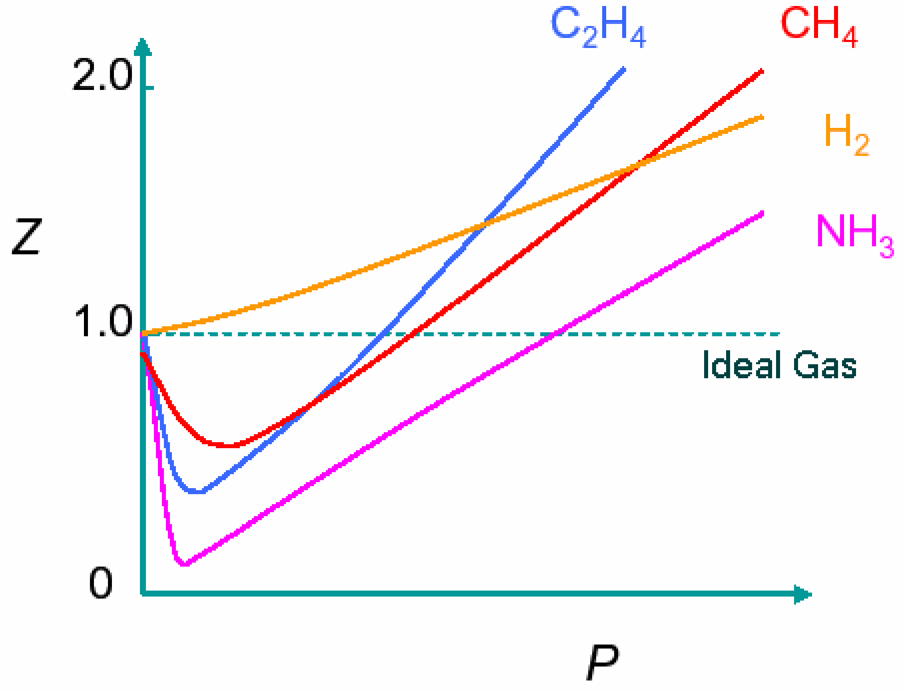
Contents:

- Compressibility Factor.
- Virial Equations
- Van der Waals Equations.
- Other Types of Equations.

Compressibility Factor also known as compression factor)

$$Z = \frac{P\overline{V}}{RT} = \frac{\overline{V}}{\overline{V}_{\text{ideal}}} \qquad (2.1)$$

The curve for each gas becomes more ideal as T ➔



Example 2.1

The density (ρ) of steam of 100.0°C and 1.01325 bar is 0.5974 kg m^{-3}.

Calculate:

i. the compressibility factor.

ii. the deviation of the volume from the ideal behaviour

Solution

i- Submitting n = m/M and ρ = m/v into (2.1)

(m = mass of the gas)

$$Z = \frac{PV}{nRT} = \frac{PMV}{mRT} = \frac{PM}{\rho RT} \qquad (2.2)$$

Example 2.1

ii-

$$Z = \frac{PV}{nRT} = \frac{PM}{\rho RT}$$

$$Z = \frac{(1.01325\ x10^{5}\ Pa)(18.0152\ x10^{-3}\ kg)}{(0.5975\ kg\ \mathrm{m}^{-3})(8.314\ m^{3} Pak^{-1} mol^{-1})(373.15\ k)} = 0.9848$$

Example 2.1

(ii) The ideal molar volume RT/P = 0.030618 m3 = 30618 m. The real molar volume from Eq. (1.3) is

$$\overline{V}\ \text{real} = \left(\frac{RT}{P}\right)Z$$

$$\overline{V}_{\text{real}} = \overline{V}_{\text{Ideal}}\,Z = 30618\text{x}0.9848 = 30152.6\ \text{L}$$

$$\text{Deviation} = \frac{\overline{V}_{ideal} - \overline{V}_{real}}{\overline{V}_{ideal}} x100 = \frac{30618 \quad - \ 301526}{30618} x\,100 \quad = 1.52\ \%$$

So this gas shows 1.52% deviation from ideal behaviour under these conditions.

Equations of Real Gases

Many equations of state have been proposed for real gases (table 2.1), derived from different theoretical models or based on different ideas about how to fit experimental PVT data on an empirical equation.

Table 2.1 *Some Two-Parameter Equations Suggested to Describe the PVT Behavior of Gases.*

Virial	$\frac{PV}{nRT} = 1 + \frac{B}{V} + \frac{C}{V^2} + ...and \qquad \frac{PV}{nRT} = 1 + B'P + C'P + ...$
Van der Waals	$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$
Berthelot	$\left(\mathrm{p} + \frac{\mathrm{n^2 aT}}{\mathrm{V^2}}\right)(\mathrm{V} - \mathrm{nb}) = \mathrm{nRT}$
Dieterici	P x e [na/(RTV)] (V-nb) = nR
Redlich-Knowing	$\left(\mathrm{p} + \frac{\mathrm{n^2 aT}}{\mathrm{V^2}}\right)(\mathrm{V} - \mathrm{nb}) = \mathrm{nRT}$

Virial Equations

Real gases have non-zero volume at low T and high P

have repulsive and attractive forces between molecules

short range,

important at high *P*

longer range,
important at moderate *P*

At low pressure, molecular volume and intermolecular forces can often be neglected, i.e. properties → ideal.

Virial Equations

Virial Equations

$$\frac{PV}{nRT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots.. \qquad (2.5)$$

$$\frac{PV}{nRT} = 1 + B'P + C'P + \ldots.. \qquad \textit{(2.6)}$$

RT is the first virial equation

B is the second virial coefficient.

C is the third virial coefficients.

They are temperature dependent.

Virial Equations

The equations have the form that makes it suitable base for the description of the PVT behavior of real gases.

The coefficients of the virial expression with pressure terms are related to those of the virial equation with volume terms.

$1/V = BRT$ and $V = B'RT$ (2.7)

Example 2.2

Calculate the molar volumes of CH_4 at 200oC and 400 bars according to the virial equations. What is the deviation from the ideal behavior? The virial coefficient B of CH_4 at 200oC is -0.417 L mol-1.

Solution

(i) $$\overline{V}_{ideal} = \frac{RT}{P} = \frac{(8.314x10^{-2}\,L\ \mathrm{bar\ K^{-1}}\,mol^{-1})(473\ \mathrm{K})}{400\ \mathrm{bar}}$$

$= 9.83 \times 10^{-2}$ L mol-1

Example 2.2

(ii) From Eq. (2.5) we have that

$$Z = 1 + BV = 1 + \frac{BP}{RT}$$

$$= 1 + \frac{(-0.417\ \mathrm{L\ mol^{-1}})(400\ \mathrm{bar})}{(8314x10^{-2}\ L\ \mathrm{bar\ K^{-1}}\ mol^{-1})(573K)} = 0.9965$$

$$\therefore \overline{V}_{real} = \overline{V}_{ideal} Z =$$ (9.83x10^{-2} mol^{-1})(0.9965)

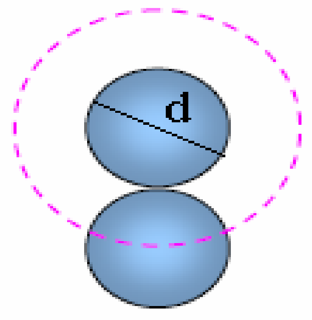
=9.79 x 10^{-2} L mol^{-1}

c) Deviation = $$\frac{9.83x10^{-2} - 9.79x10^{-2}}{9.83x10^{-2}} x100 = 0.4\%$$

Van der Walls Equations

van der Waals attributed the failure of the PV = nRT to

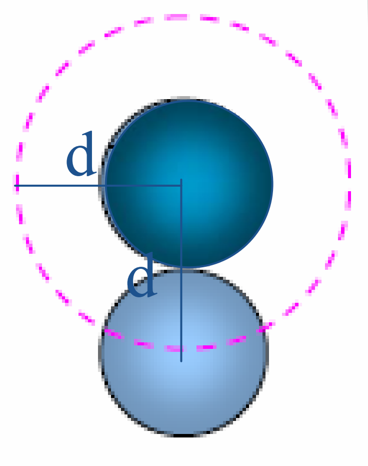
- the volume occupied by the gas molecules and



- the attractive forces between the molecules.

Excluded Volume

- Instead of treating gas molecules as mass points, van der Waals treated them as rigid spheres of diameter d.



- The nearest approach of the center of one molecule to the center of another molecule of the same species is also **d**.

- Thus for each pair of molecules a volume of $4/3\ \pi d^3$ is excluded.

  We thus obtain

Excluded Volume

Thus we obtain that

Excluded volume per a molecule = V_{exc}

V_{exc} = ½ (4/3 πd^3) = 4[1/8(4/3 πd^3)] = 4[4/3 $\pi (d/2)^3$]

The expression in brackets is the volume of a molecule.

V_{exc}= 4 times the actual volume of a molecule

Excluded volume for N_A molecules = 4 times the actual volume of N_A molecules

Excluded Volume

If the total excluded volume for N_A molecules (Avogadro's number) is b, then

$$b = 4 N_A \left[\frac{4}{3} \pi \left(\frac{d}{2} \right)^3 \right] \qquad (2.8)$$

where b is a constant for given species of a gas.

$V_{real} = V_{ideal} - nb$

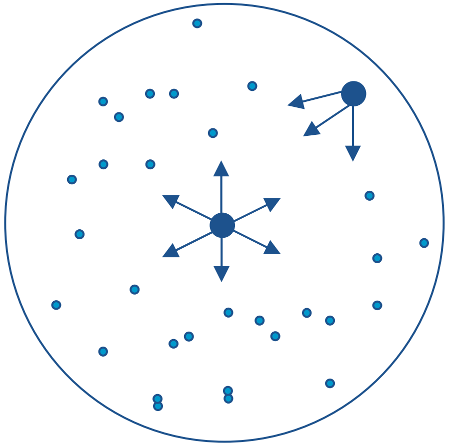
This correction modifies the ideal-gas equation to

$P(V-nb) = nRT$

Molecular Attraction

Van der Waals made the correction for attractive forces as follows.

- Attraction occurs between pairs of molecules,
- Molecular attraction decreases the number of collisions on the walls of the container (n/V)
- Attraction forces increases as the number of molecules increases in the container (n/V)
- Attraction forces should proportional with the square of the concentration of molecules, $(n/v)^2$.
- Attractive forces = $a(n/V)^2$



Molecular Attraction

The real pressure P will be less than the ideal-gas pressure by an amount $a(n/v)^2$, where a is a different constant per each gas.

or $P_{real} = P_{ideal} - a(n/V)^2$

The result of both the van der Waals corrections is, therefore

Molecular Attraction

$$\left(P + a\left(\frac{n^2}{v^2} \right) \right)(V - ab) = nRT \qquad (2.10)$$

or

$$P = \frac{\mathrm{nRT}}{\mathrm{v} - \mathrm{nb}} - \frac{\mathrm{an}^2}{\mathrm{v}^2} \qquad (2.11)$$

If n = 1, we have that

$$(P + \frac{a}{\overline{V}^2})(\overline{V} - b) = RT \qquad (2.13)$$

The van der Waals Eqs. (2.10 and 2.11) represents the PVT behavior of gases quite well when they deviate moderately from ideality.

Example 2.3

Calculate the pressure needed to confine 1 mol of carbon dioxide gas to a volume of 0.5 L at 298 K using van der Waals equation. Estimate the radius of CO_2 molecule.

$a = 3.592\ L^2$ atm mol^{-2} and $b = 0.0427$ L mol^{-1}.

Pressure of CO_2

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

Since V =0.5 L and T = 298 K, then R = 0.082 L atm K^{-1} .mol^{-1}

$$P_{real} = \frac{(0.082\,\mathrm{L\,atm\,K^{-1}}\,mol^{-1})(298K)}{0.5L\,\mathrm{mol^{-1}} - 0.0427\,\mathrm{L\,mol^{-1}}} - \frac{3.592\,\mathrm{L}^2 atm\,\mathrm{mol^{-2}}}{(0.5\,\mathrm{L\,mol^{-1}})^2}$$

Example 2.3

P_{real} = 48.87 atm – 7.18 atm = 41.69 atm.

P_{ideal} = nRT / V = 1 x 0.082 x 298 / 0.5 = 48.87 atm

The pressure is appreciably less 7 atm than that would be needed if carbon dioxide behaved ideally.

Radius of CO_2

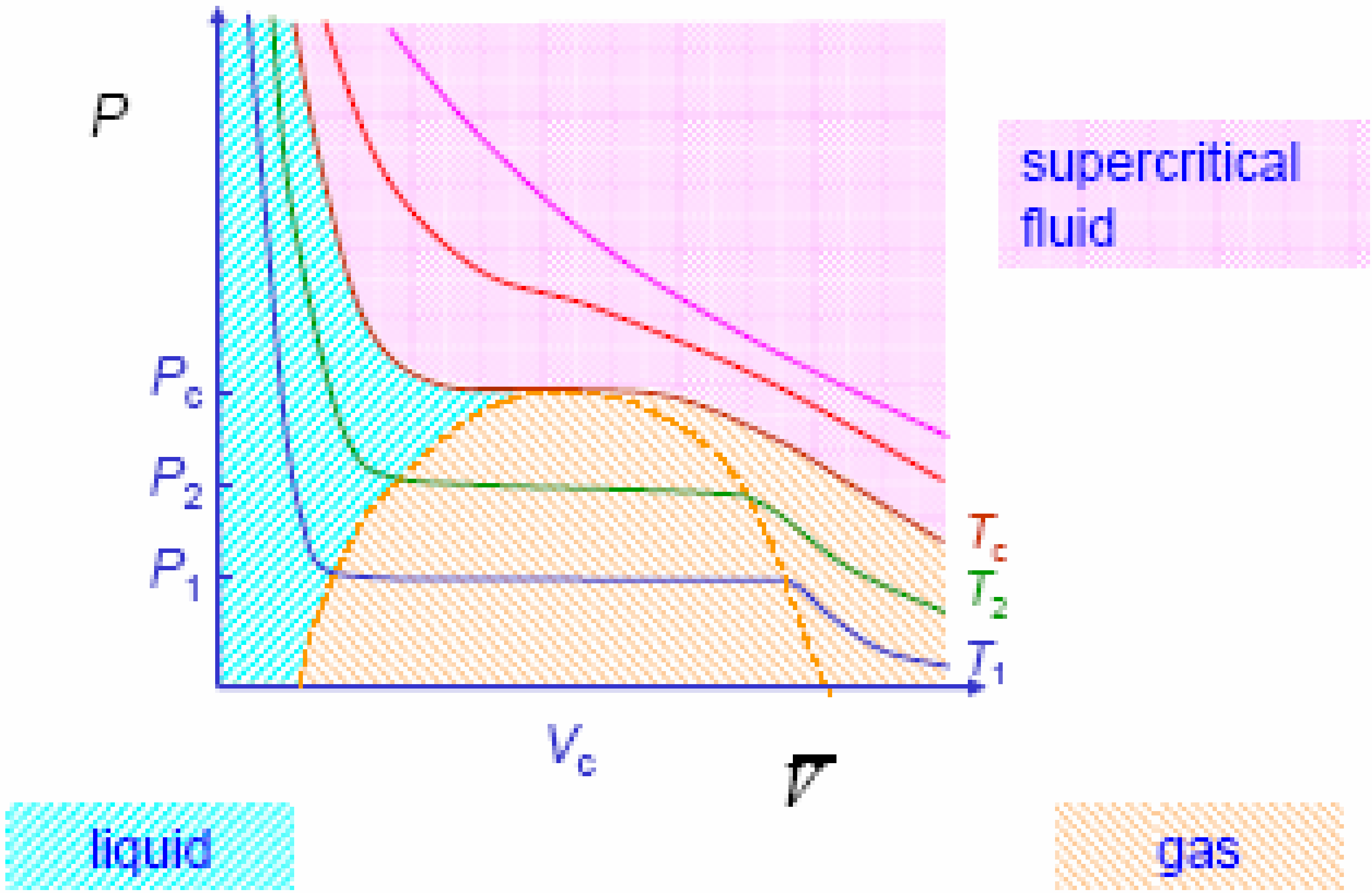
$$\because b = 4\mathrm{N_A}\left[\frac{4}{3}\pi\left(\frac{d}{2}\right)^3\right] = 4N_A\pi r^3$$

$$\therefore r^3 = \frac{b}{4N_A\pi} = \frac{0.0427x10^{-3}}{4x6.02x10^{23}\pi} = 5.64x10^{-30}\ m^3$$

$r = 2.15 \times 10^{-10}$ m

The pressure is appreciably less than the 100 bar that would be needed if methane behaved ideally.

Condensation of Gases



The constants of van der Waals equation can be evaluated from critical-point data.

- T_c is the critical temperature which is defined as the highest temperature at which liquid and vapor can exist together (condensation of the gas is possible) .

- P_c is the pressure at which condensation of vapor to liquid occurs when the temperature is equal to T_c or the highest pressure at which liquid will boil when heated.
- V_c is the volume of a mol of the substance at T_c and P_c

The constants of van der Waals equation can be evaluated from critical-point data.

- T_c, P_c and V_c are the critical constants of the gas.
- Above the critical temperature the gas and liquid phases are continuous, i.e. there is no interface.
- Van der Waals equation, or any of the other two-parameter equations of Table 2.1, cannot describe the detained PV behavior of a gas in the region of liquid-vapor equilibrium.

The constants of van der Waals equation can be evaluated from critical-point data.

- The constants of van der waals equation can be evaluated from critical point data. The van der Waals Equation is not exact, only a model.

Applying equation (2.13) to the point of inflction at the critical point, we have that

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

(2.13)

$$\frac{dP}{d\overline{V}}=+\frac{-RT}{(\overline{V}-b)^2}+\frac{2a}{\overline{V}^3}=0$$

(2.14)

and

$$\frac{d^2P}{d\overline{V}^2}=\frac{2RT}{(\overline{V}-b)^3}-\frac{6a}{\overline{V}^4}=0$$

(2.15)

The constants of van der Waals equation can be evaluated from critical-point data.

- These three equations can be solved for a, b, and R in terms of P_C, V_C, and T_C. to obtain that

$$b = \frac{1}{3} V_C \qquad a = 3P_C V_C^2 \qquad R = \frac{8P_C V_C}{3T_C} \qquad (2.15)$$

- The last of these equations can be rearranged to get the compressibility factor at the critical point,

$$Z = \frac{P_C V_C}{RT_C} = \frac{3}{8} \qquad (2.16)$$

The constants of van der Waals equation can be evaluated from critical-point data.

- ☐ The values of a and b are often chosen so that the van der Waals PV isotherm with a horizontal point of inflection occurs at P_c and T_c.

- ☐ This procedure can be followed by eliminating the V_C term, by using $V_C = 3b$, from the other expression of Eq. (2.15). The resulting expressions for a and b are

$$a = \frac{27\ \mathrm{R}^2 T_C^2}{64\ \mathrm{P}_\mathrm{C}} \quad and \quad b = \frac{RT_C}{8P_C} \qquad (2.17)$$

The constants of van der Waals equation can be evaluated from critical-point data.

The compressibility factor of some gases at the critical point

Gas	$\frac{P_C V_C}{RT_C}$
H_2	0.33
He	0.32
CH_4	0.29
NH_3	0.24
N_2	0.29
O_2	0.29

Example 2.5

Evaluate the van der Waals constants for O_2 using

T_C = -118.4^{0}C and P_C = 50.1 atm.

Using Eq. (2.17) gives that

$$a = \frac{27R^2T_C^2}{64P_C} = \frac{27(0.082)\text{ L atm K}^{-1}mol^{-1})^2(154.8\text{ K})^2}{64(50.1\text{ atm})} = 1.360\ L^2atm\ \text{mol}^{-2}$$

$$\text{b} = \frac{\text{RT}_\text{C}}{8\text{P}_\text{C}} = \frac{(0.082\text{ L atm K}^{-1}\text{ mol}^{-1})^2(154.8\text{ K})^2}{8(50.1\text{ atm})} = 0.0317\ \text{L}^2\text{atm mol}^{-2}$$

Van der Waals Equation and The Principle of Corresponding States

Analysis of the critical point data indicated that

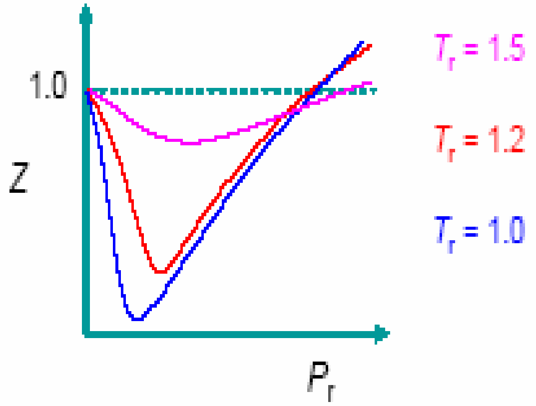
- The compressibility factor has nearly the same value for all gases at the critical point.
- At the critical point, all gases are equally non-ideal.
- It will be convenient to introduce variables that relate P, V and T to the value of these variables at the critical point.
- To do this define the ratio of P, V and T to the critical values P_C, V_C and T_C, respectively, as the reduced variables

$$P_R = P/P_C \qquad V_R = V/V_C \qquad T_R = T/T_{C-}$$

Van der Waals Equation and The Principle of Corresponding States

- ✓ J.H. Van der Waals pointed out that, to fairly good approximation at moderate pressures, all gases follow the same equation of state in terms of reduced variables.
- ✓ He called this rule the ***principle of corresponding states.***
- ✓ This behavior is illustrated for a number of different gases.

Since this is independent of *a* and *b*, all gases follow the same curve (approximately).



- Introducing the reduced variables P_R, V_R, and T_R into the van der Waals Eq gives that

$$\left(P_R + \frac{3}{V_R^2}\right)\left(V_R - \frac{1}{3}\right) = \frac{8}{3}T_R \qquad (2.18)$$

- In this form, van der Waals equation requires no quantities that characterize a particular gas – other than the critical-point data implicit in the reduced variables.
- Thus van der Waals equation is consistent with the law of corresponding states.

Quiz 2

2.1. Why gases deviate from the ideal behavior ?

2.2. At what conditions gases can follow the ideal gas equation?

2.3. Define the terms;

(i) compressibility factor, (ii) excluded volume,

(iii) critical point and (iv)reduced variables.

2.4. Why the compressibility factor is important?

2.5. Give examples of real gas equations.

2.6. Show how van der Waals corrects the ideal gas equation for real gases.

Theory of Gases

- Kinetic Theory of Gases
- Equations of Real Gases
- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases

Distribution of Velocities of Gas Molecules in One Direction (Boltzmann Distribution)

According to the model on which the kinetic-molecular theory is based, the molecules of a gas are moving with a variety of speeds and directions, i.e., with various velocities.

Distribution of Velocities of Gas Molecules in One Direction (Boltzmann Distribution)

Since gases behave similarly in all directions,

- We will investigate the distribution along a particular direction, say the x direction.

We assume that we have a sample of a gas of:

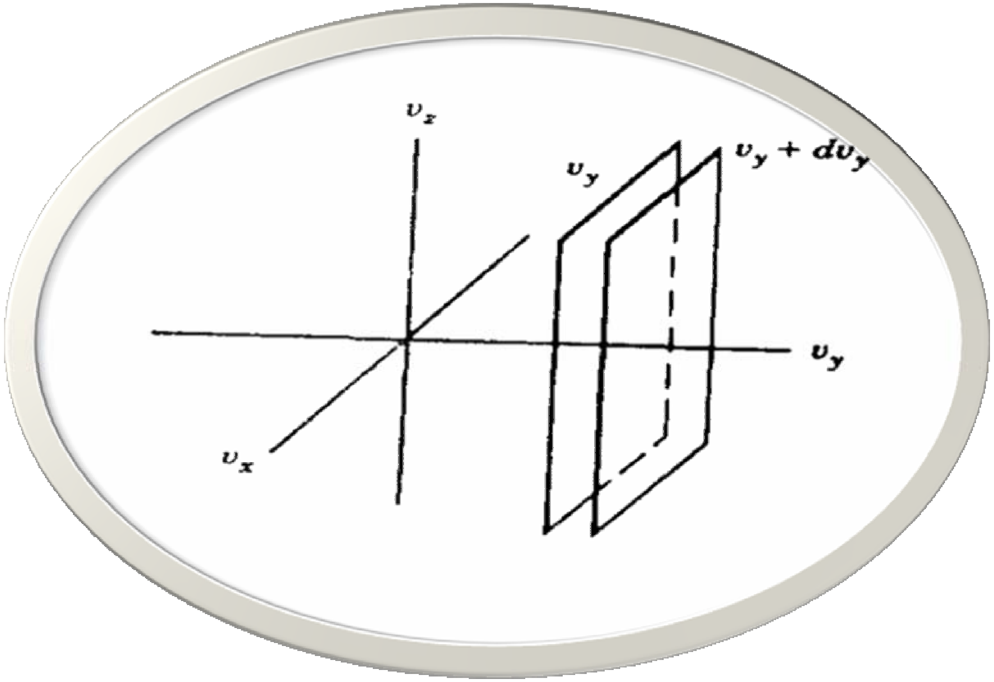
N total number of molecules .

dN probable number of molecules of velocities in the x direction between U_x and $U_x + dU_x$

dN/N fraction of molecules of velocities between U_x and $U_x + dU_x$ or the probability of finding molecules between the two planes.

Distribution of Velocities of Gas Molecules in One Direction (Boltzmann Distribution)

This is also the probability of finding molecules with velocity components between two planes



Distribution of Velocities of Gas Molecules in One Direction (Boltzmann Distribution)

- The probability is expressed also as f(u_x) du_x component .

For each molecule $\varepsilon = ½ mU_x^2$

According to the Boltzmann distribution expression,

$$\frac{dN}{N} \alpha\, e^{-(1/2)mu_x^2/kT} du_x \qquad \therefore \frac{dN}{N} = Ae^{-(1/2)mu_x^2/kT} du_x \qquad (3.1)$$

- This constant can be evaluated by recognizing that integration of the right side of Eq. (3.1) over all possible values of u_x, that is, from **$u_x = -\infty$ to $u_x = +\infty$**, must account for all the velocity points. Thus we can write

$$A\int_{-\infty}^{+\infty} e^{-(1/2)mu_x^2/kT}\, \mathrm{du}_x = 1 \qquad (3.2)$$

Gas Molecules Simulation

- so that the proportionality constant A is given by

$$A = \frac{1}{\int_{-\infty}^{+\infty} e^{-(1/2)mu_x^2/kT}} du_x \qquad (3.3)$$

- The value of the integral is seen from the table of integrals to be $\sqrt{2\pi kT/m}$, and we obtain

$$A = \sqrt{\frac{m}{2\pi kT}} \qquad (3.4)$$

Gas Molecules Simulation

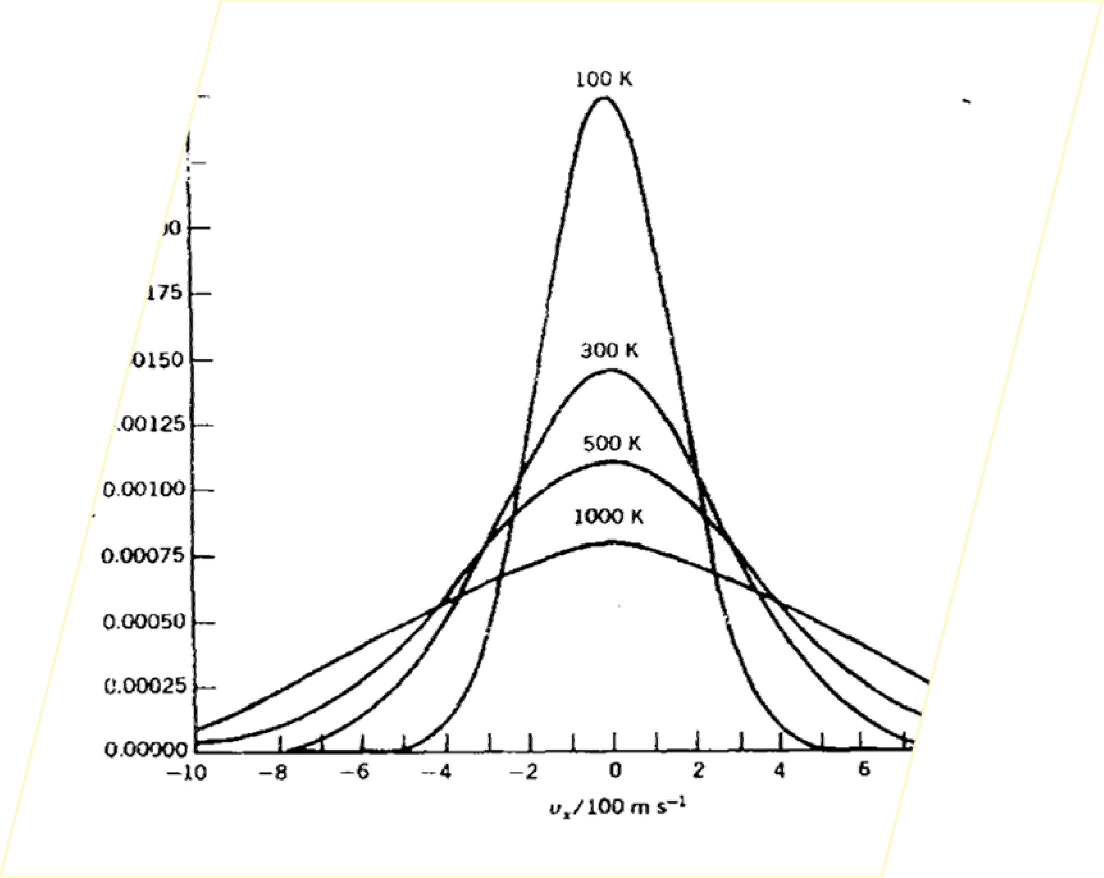
- Finally, the equation for the distribution over the velocities along the x direction for a sample of N molecules can be written as

$$f(u_x) = \frac{dN/N}{dU_X} = \left(\frac{M}{2\pi RT}\right)^{1/2} \exp\left(-\frac{mu_x^2}{2RT}\right) \qquad (3.5)$$

•Note that **f(u_x)** is a velocity **probability density** so that the probability of finding a molecule with velocity components between u_x and u_x+ du_x is given by **f(u_x)du_x**.

•Graphs of this one-dimensional distribution function can be obtained

Gas Molecules Simulation



Probability density $f(U_x)$ for the velocity of oxygen molecules in an arbitrarily chosen direction at 100, 300, 500, and 1000 K.

Example 3.1

Calculate the probability density for u_x of N_2 molecules at 300 K.

Using equation (3.5)

$$f(u_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} \exp\left(-\frac{mu_x^2}{2RT}\right)$$

$$= \left[\frac{0.028 g\,\mathrm{mol}^{-1}}{2\pi(8.314 JK^{-1} mol^{-1})(300K)}\right]^{1/2} \exp\left[-\frac{(0.028 g\ \mathrm{mol}^{-1})(300 ms^{-1})^2}{2(8.314 JK^{-1} mol^{-1})(300K)}\right]$$

$= 8.065 \times 10^{-4}$ s m^{-1}

Exercise
Calculate the probability density of N2 at 0 and 600 K.

Maxwell – Boltzmann Distribution
(in three dimensions)

- The speed u of a molecule is related its component velocities by

$$u^2 = u_x^2 + u_y^2 + u_z^2 \qquad (3.6)$$

- Therefore, F(u) du is the probability of finding a molecule with a speed between u and u + du .
- The one-dimensional distribution can be combined to give the fraction of the molecules that have velocity components between u_x and $u_x + du_x$, u_x and $u_y + du_y$ and u_z and $u_z + du_z$.

Maxwell – Boltzmann Distribution
(in three dimensions)

- It is given analytically ;

$f(u_x, u_y, u_z)\, du_x du_y, du_z = \dfrac{dN}{N}$

$$\therefore \frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}\left(u_x^2 + u_y^2 + u_z^2\right)\right] du_x du_y du_z \qquad (3.7)$$

- The probability of finding a molecule with velocity components between u and u+ du is given by

$$F(u)du = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right) du \qquad (3.8)$$

Maxwell – Boltzmann Distribution
(in three dimensions)

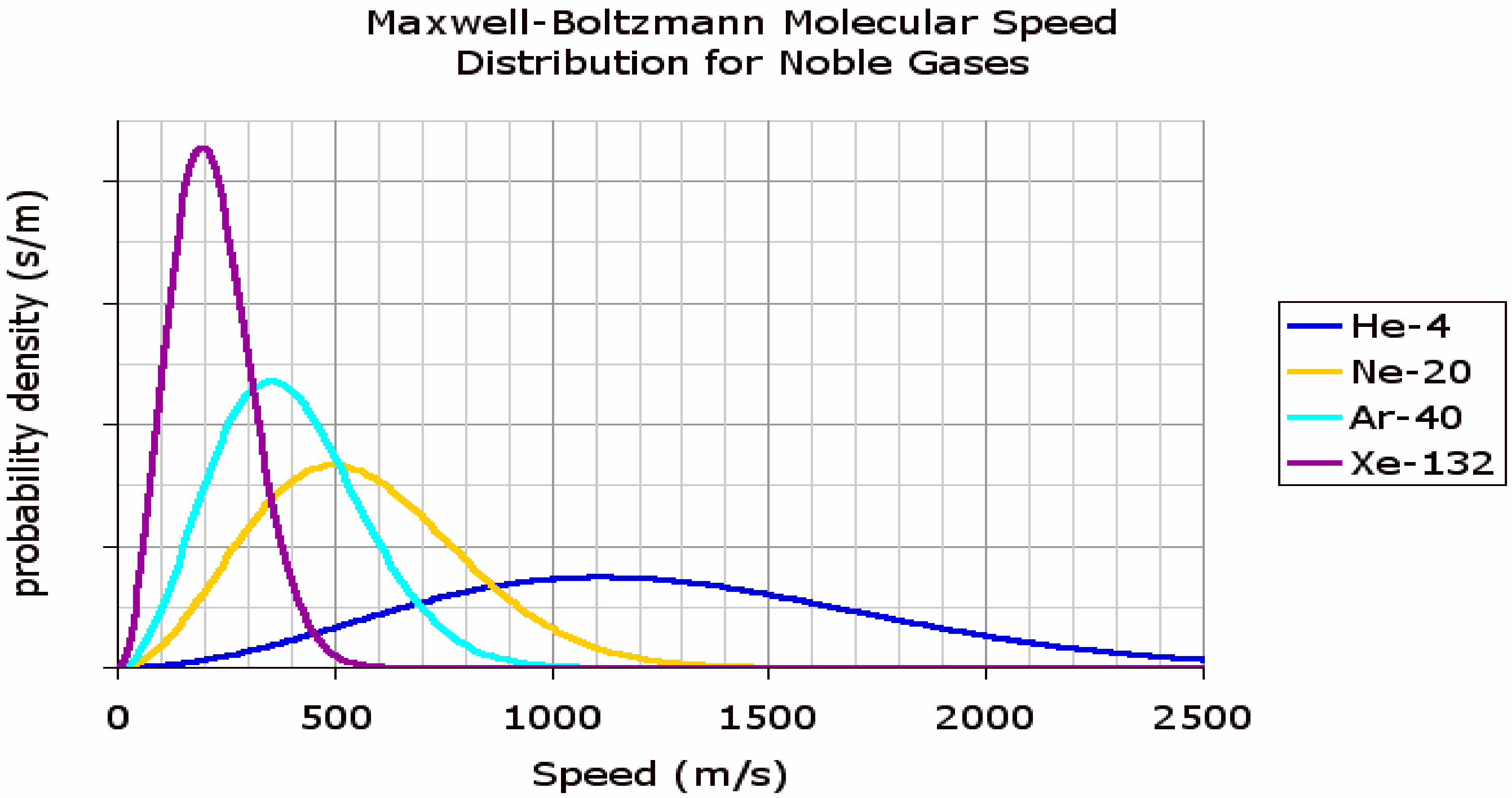
- The probability density F(u) is

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right) \qquad (3.9)$$

- The probability density at a speed of 0 is zero.

- The probability density increases with the speed up to a maximum and then declines.

Maxwell – Boltzmann Distribution
(in three dimensions)



Example 3.2

A flask contains of N_2 molecules at 100 K. How many molecules have a velocity in the range 500.0-500.1 ms^{-1}?

Suppose that we have a sample of 1 mol of N_2

$$\frac{dN}{N_A} = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mu^2}{2kT}\right) du$$

$$= 4\pi(500 ms^{-1})^2 \left(\frac{(4.65x10^{-26} kg)(T/kgm^2 s^{-2})}{2\pi(1.381x10^{-23} JK^{-1})(100K)}\right)^{1/2}$$

$$Exp\left(-\frac{(4.65x10^{-26} kg)(500 ms^{-1})^2 (J/kgm^2 s^{-1})}{2\pi(1.38x10^{-23})(JK^{-1})(100K)}\right)(0.1 \text{ ms}^{-1})$$

$$\frac{dN/N_A}{du} = 5.79x10^{-4} sm^{-1}$$

Example 3.2

The number of molecules have velocities in the range 500.0-500.1 ms^{-1}

dN = (5.79x10-4)(6.022x1023)(0.1) = 3x1019 molecules

and the percent of them is given as follows:

$$\frac{dN}{N}x100 = \frac{3x10^{19}}{6.02x10^{23}}x100 = 4.98x10^{-3}\%$$

Exercise

How much is the % of O_2 molecules have velocities in the range between 300 – 300.1 ms^{-1}?

Theory of Gases

- Kinetic Theory of Gases
- Equations of Real Gases
- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases

Speeds of Gas Molecules

The speed of gas molecules is of three types

- Most Probable Speed (u_p)
- Mean (average) Speed ($\bar{u}$)
- Root mean-square Speed (u_{rms}).

Speeds of Gas Molecules

Most probable speed u_p :

It is the speed at the maximum of F(u). Differentiating Eq. 3.9 and setting dF/du equal to zero, we find

$$\frac{dF(u)}{du}=\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-mu^2/2kT}\left[8\pi u+4\pi u^2\left(-\frac{mu}{kT}\right)\right]=0$$

$$\therefore u_p=\left(\frac{2kT}{m}\right)^{1/2}=\left(\frac{2RT}{M}\right)^{1/2} \qquad (4.1)$$

Speeds of Gas Molecules

Mean speed ($\bar{u}$):

It is calculated as the average of (u) using the probability distribution F(u):

$$\bar{u} = \int_0^\infty uF(u)\,du$$

Substituting Eq.(3.9) and performing the integral with the help of tables, we find

$$\bar{u} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty \exp\left(-\frac{mu^2}{kT}\right)u^2 du$$

$$\therefore \bar{u} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2} \qquad (4.2)$$

Speeds of Gas Molecules

Root-mean square speed (u_{rms}):

Which is defined as the square root of $\overline{u^2}$

$$u_{rms} = (\overline{u^2})^{1/2} = \left[\int_0^\infty u^2 F(u)\,du\right]^{1/2}$$

Substituting Eq. 3.9 and using tables again, we find

$$u_{rms} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2} \qquad (4.3)$$

Speeds of Gas Molecules

From these three calculations,

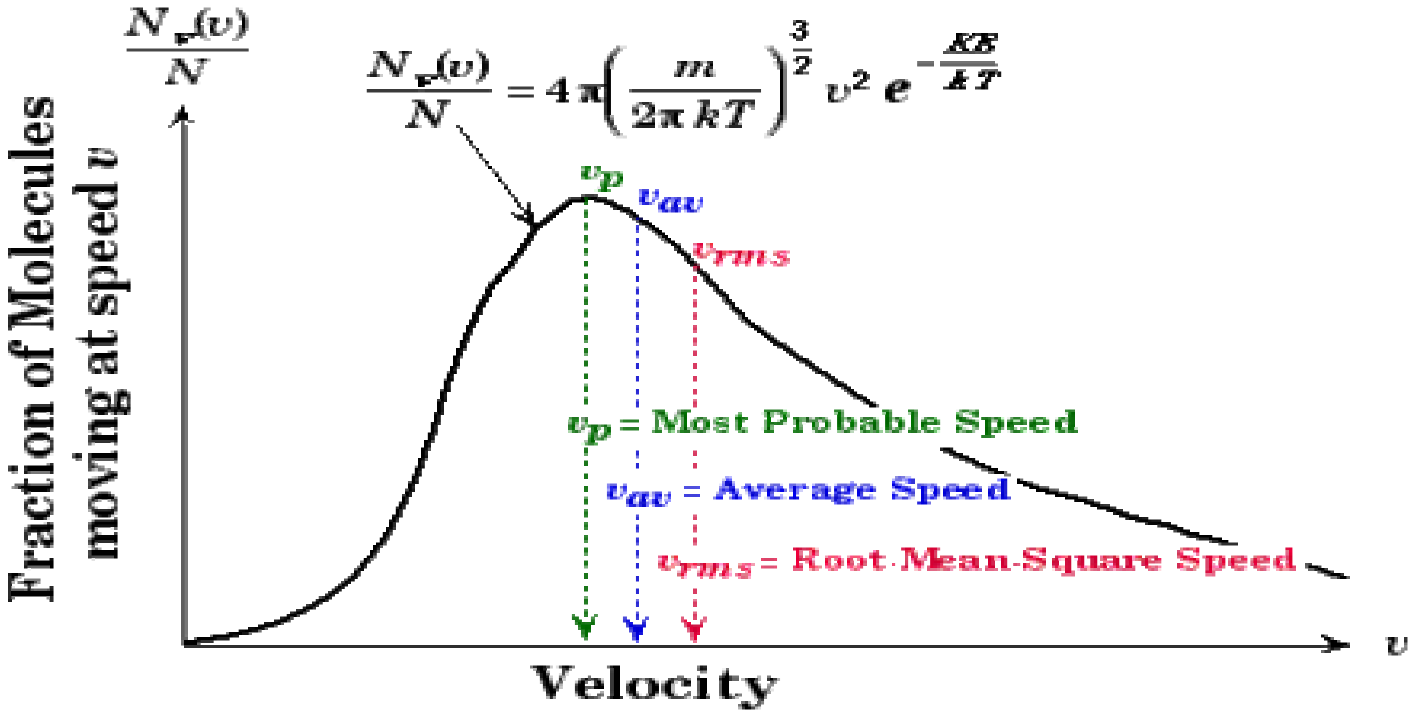
$$u_p = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

$$\overline{u} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

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

We can see that at any temperature $u_{rms} > \overline{u} > u_p$

Molecular Collision



$$v_p = \sqrt{2\frac{kT}{m}} \qquad v_{av} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \qquad v_{rms} = \sqrt{3\frac{kT}{m}}$$

Speeds of Gas Molecules

✓ Each of these speeds is proportional to $(T/M)^{1/2}$.

✓ Each increases with temperature

✓ Each decreases with molar mass. Lighter molecules therefore move faster than heavier molecules on average, as shown in the following table.

Speeds of Gas Molecules

Various types of average speeds of gas molecules

Gas	$(u^2)^{1/2}$/m s^{-1}	(u)/m s^{-1}	u_p/m s^{-1}
H_2	1920	1769	1568
O_2	482	444	394
CO_2	411	379	336
CH_4	681	627	556

Example 4.1

Calculate the The different types of speeds of hydrogen molecules at 0°C.

$$u_p = \left(\frac{2RT}{M}\right)^{1/2} = \left[\frac{(2)(8.314\ Jk^{-1}mol^{-1})(273\ k)}{(2.016\ x10^{-3}\ kg\ \mathrm{mol}^{-1})}\right]^{1/2} = 1.50 \text{ x } 10^{3} \text{ m s}^{-1}$$

$$\bar{u} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{(8)(8.314\ Jk^{-1}mol^{-1})(273\ k)}{(3.146)(2.016\ x10^{-3}\ kg\ \mathrm{mol}^{-1}}\right]^{1/2} = 1.69 \text{ x } 10^{3} \text{ m s}^{-1}$$

Example 4.1

$$u_{rms} = \left(\frac{3RT}{M}\right)^{1/2} = \left[\frac{3(8.314 Jk^{-1} mol^{-1})(273.15k)^{1/2}}{2.06x10^{-3}\,kg\,\mathrm{mol}^{-1}}\right] = 1.84 \text{ x } 10^{3} \text{ m s}^{-1}$$

The root-mean square speed of a hydrogen molecule at 0°C is 6620 kmh^{-1}, but at ordinary pressures it travels only an exceedingly short distance before colliding with another molecule and changing direction.

Exercise

How many molecules have a velocity exactly equal to 500 ms^{-1}?

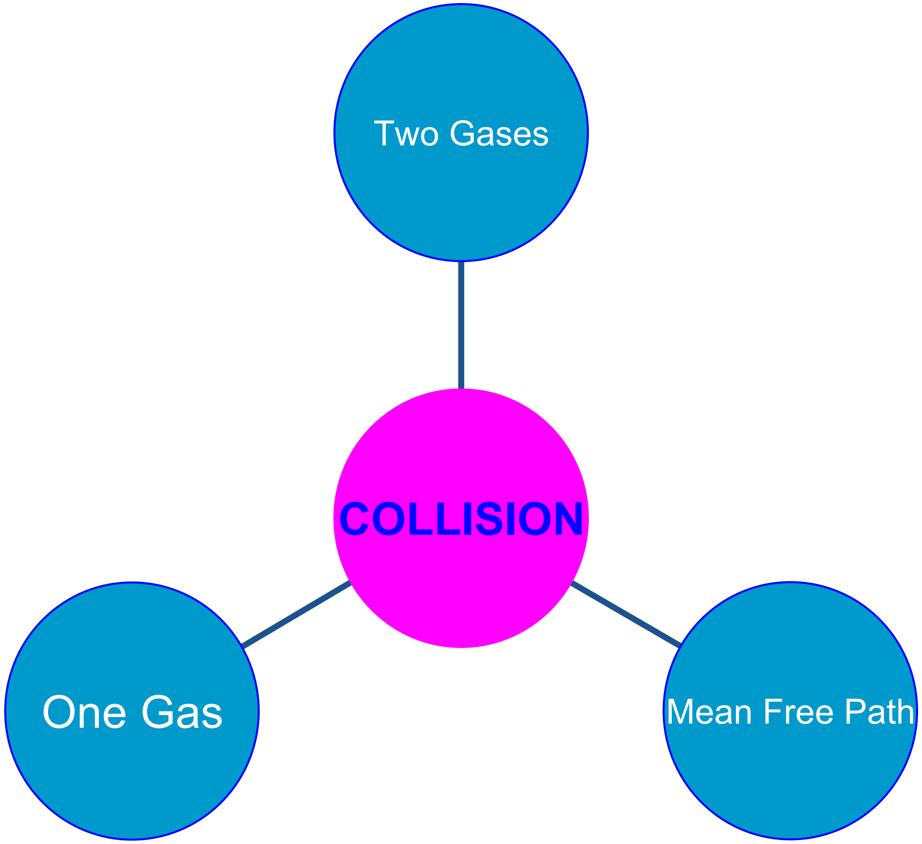
Theory of Gases

- Kinetic Theory of Gases
- Equations of Real Gases
- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases

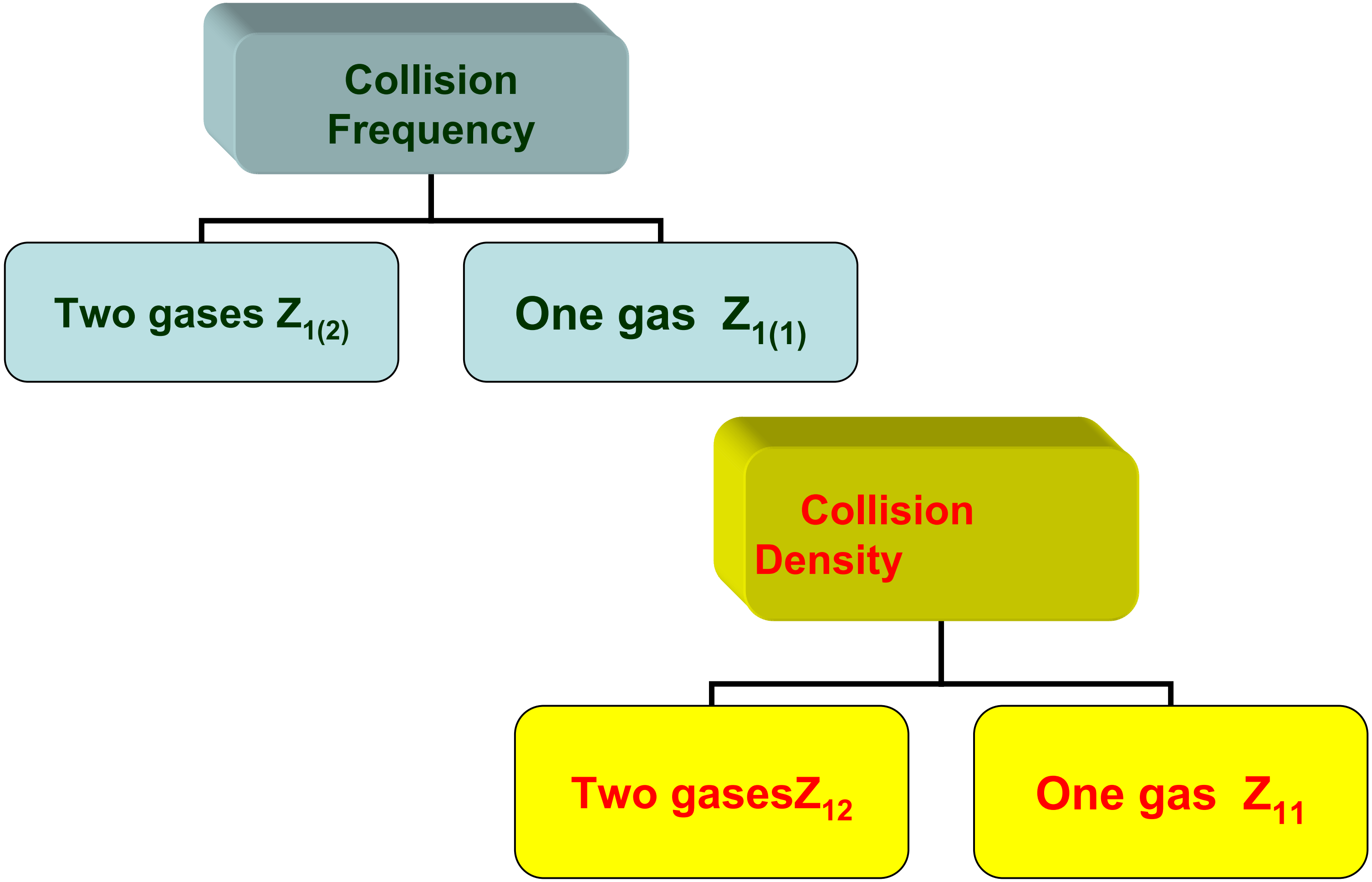
Molecular Collision

COLLISION PROPERTIES OF GAS MOLECULES

Molecular Collision



Molecular Collision



- **Collision Frequency**
  - **Two gases $Z_{1(2)}$**
  - **One gas $Z_{1(1)}$**
- **Collision Density**
  - **Two gasesZ_{12}**
  - **One gas Z_{11}**

Molecular Collision

Collision Frequency:

- The collision frequency is ***the number of collisions of molecules per unit time***, where
  - $Z_{A(B)}$ for the collision between the molecules of two different gases A and B.
  - $Z_{A(A)}$ for collision between identical molecules.
- let us consider a cylinder of length l (m) containing N_A and N_B molecules of gas A and gas B, respectively. These molecules have;
  - Diameters d_A and d_B (m) and collision diamete

$$d_{AB} = (d_A + d_B)/2 \qquad (5.1)$$

  - Atomic masses m_A and m_B (kg), molecular masses M_A and M_B (kg) and reduced mass .

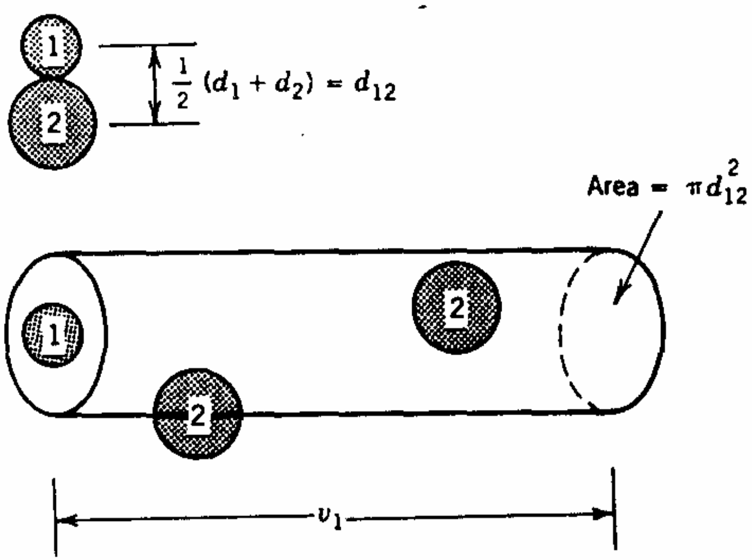
$$\mu = \frac{1}{m_A} + \frac{1}{m_B} = \frac{N_A}{M_A} + \frac{N_A}{M_B} = N_A \frac{M_A + M_B}{M_A M_B} \qquad (5.2)$$

- Densities ρ_A and ρ_B (m^{-3}), number of molecules per unit volume or $\rho = N/V$
- Velocities u_A and u_B (ms^{-1}) and mean relative velocity

$$\overline{u_{AB}} = \left(\frac{8RT}{\pi\mu}\right)^{1/2} \qquad (5.3)$$

Molecular Collision

Click here to see Flash file



☐ hard spherical molecules collide with each other if their centers come within a distance

$d_{AB} = \frac{1}{2}(d_A + d_B)$, **the collision diameter.**

Collision of different molecules

- Molecules of type B are stationary.
- A molecule of type A will collide in unit time with all molecules of type B that have their centers in a cylinder of

Volume = $\pi d_{AB}^{2} u_{A}$

- A molecule of type A would undergo a

number of collisions = $\pi d_{AB}^{2} u_{A} \rho_{B}$

per unit time.

- Molecules of type B are actually not stationary and so the relative speed $\mathbf{u_{AB}}$ should be used in calculating the rate of collisions $\mathbf{z_{A(B)}}$ of a molecule of type A with molecules of type B. Thus,

$$Z_{A(B)} = \pi d_{AB}^{2}\bar{u}_{AB}\rho_{B} \qquad (5.4)$$

or

$$Z_{A(B)} = \pi d_{AB}^{2}\left(\frac{8RT}{\pi\mu}\right)^{1/2}\rho_{B} \qquad (5.5)$$

- where $\mathbf{z_{A(B)}}$ is the **collision frequency** of molecules of type A with molecules of type B .

Molecular Collision

- The collision diameter $\mathbf{d}_{AB}$ has the unit m,
- The relative mean speed ($\mathbf{u}_{AB}$) has the unit m s^{-1},
- The collision frequency has the unit s^{-1}.

Collision Frequency of Identical Molecules

- Now a molecule of type A is moving through molecules of type A, rather than molecules of type B, Eq. (5.4) becomes

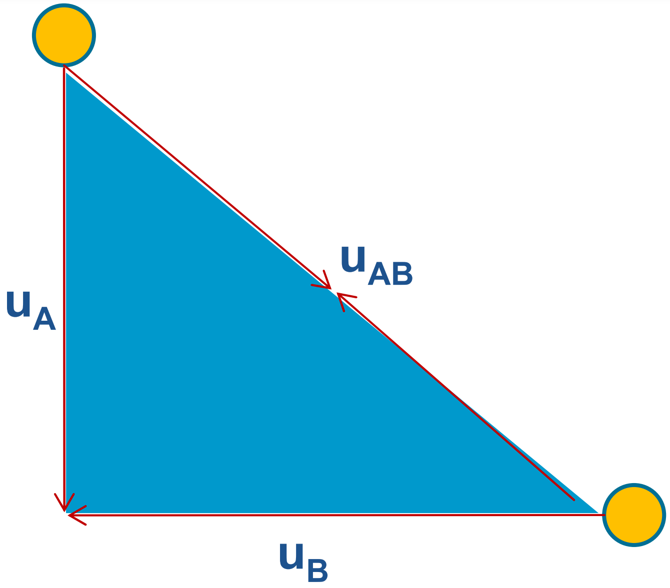
$$Z_{A(A)} = \pi d_A^2 \bar{u}_A \rho_A \qquad (5.6)$$

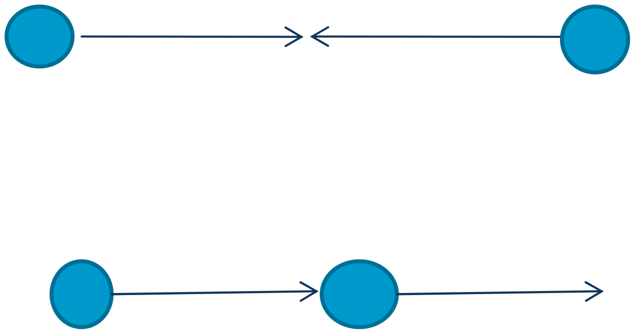
Or

$$Z_{A(B)} = \pi d_{AB}^2 \left(\frac{8RT}{\pi\mu} \right)^{1/2} \rho_B \qquad (5.7)$$

Collision Frequency of Identical Molecules

- The Pythagorean theorem can be used to interpret the mean relative speed in terms of the mean speeds of molecules A.
- They can collide with each other with any angle between 0° and 180° between their paths, but Eq. (5.7) shows that the average collision is at 90°.





Molecular Collision

The mean relative speed:

$$\bar{u}_{12} = \left(\frac{8kT}{\pi\mu}\right)^{1/2}$$

Reduced mass $\mu = m_1 m_2/(m_1+m_2)$.

$$(\bar{u}_{12})^2 = \left(\frac{8kT}{\pi}\right)\left(\frac{1}{m_1} + \frac{1}{m_2}\right) = (\bar{u}_1)^2 + (\bar{u}_2)^2$$

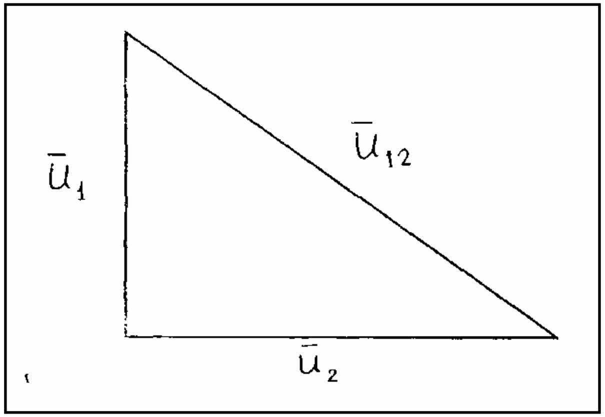
$$z_{1(2)} = \rho_2 \pi \, \mathrm{d}_{12}^2 \, \bar{\mathrm{u}}_{12} = \rho_2 \pi \, \mathrm{d}_{12}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2}$$

Molecular Collision

In case of one type of molecules

$$\overline{u}_{11}^{\,2} = 2\,\overline{u}_{1}^{\,2}$$

$$\overline{\mathbf{u}}_{12} = \sqrt{2\,\mathbf{u}_{1}} = \sqrt{2}\;\overline{\mathbf{u}}$$



d^2□□$z_{1(1)}$ = $2^{1/2}$

d^2 □□= $2^{1/2}$

$$\overline{u} = \left(\frac{8\mathbf{kT}}{\pi\mu}\right)^{1/2}$$

Molecular Collision

The collision frequency z1(1) is thus ,

* The rate of collisions of a molecule of a gas with molecules of the same gas.

* The number of collision of one molecule of a gas with molecules   of the same gas per unit time per unit volume

Example 3.1

What is the mean relative speed of **H_2** molecules with respect to **O_2**molecules (or oxygen molecules with respect to hydrogen molecules) at 298 ?

Example 3.1

The molecular masses are:

$$m_1 = \frac{2.016\,x10^{-3}\,kg\ mol^{-1}}{6.022\,x10^{23}\ mol^{-1}} = 3.348\,x10^{-27}\,kg$$

$$m_2 = \frac{32.00\,x10^{-3}\,kg\ mol^{-1}}{6.022\,x10^{23}\ mol^{-1}} = 5.314\,x10^{-26}\,kg$$

$$\mu = [(3.348x10^{-27}\,kg0^{-1} + (5.314x10^{-26}\,kg)^{-1}]^{-1} = 3.150x10^{-27}$$

$$\bar{u}_{12} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} = \left[\frac{8(1.381\,x10^{-23}\ Jk^{-1})(298\,k)}{\pi(3.150\,x10^{-17}\,kg)}\right] = 1824\ m\ s^{-1}$$

Example 3.1

Note that the mean relative speed is closer to the mean speed of molecular hydrogen (1920 ms^{-1}) than to that of molecular oxygen (482 ms^{-1}) .

Collision Density

It is the number of collisions per unit tim per unit volume.

For two gases:

To calculate the number of collisions of molecules of type 1 with molecules of type 2 per unit time per unit volume of gas

z12 = z1(2)_x ρ1

z12 = ρ1ρ2π d21212

Collision Density

z_{11}/mol L^{-1}s^{-1}		$z_{1(1)}$/s^{-1}		
10^{-6} bar	1 bar	10^{-6} bar	1 bar	Gas
2.85x10^{-4}	2.8x10^{8}	14.13x10^{3}	14.13x10^{9}	H_2
1.26x10^{-4}	1.26x10^{8}	6.24x10^{3}	6.24x10^{9}	O_2
1.58x10^{-4}	1.58x10^{8}	8.81x10^{3}	8.81x10^{9}	CO_2
2.08x10^{4}	2.08x10^{8}	11.60x10^{3}	11.69x10^{9}	CH_4

For one gas only :

The number of collisions of molecules of type 1 with other molecules of type 1 per unit time per unit volume of gas will be reduced to

$$z11 = ½\ \rho 2\pi d2\bar{u}\ 11$$

$$1/2 = 2\text{-}1/2 \quad = 1/\ \surd 2$$

or $$z11 = 2\text{-}1/2\ \rho 2\pi d2\ \bar{u}$$

For one gas only :

where a divisor of 2 has been introduced so that each collision is not counted twice and 11 has been placed by 21/2 by means of the reduced mass of like particles.The collision density is readily expressed in mol m-3s-1 by simply dividing by the Avogadro constant.

For one gas only :

where a divisor of 2 has been introduced so that each collision is not counted twice and 11 has been replaced by 21/2 by means of the reduced mass of like particles. The collision density is readily expressed in mol m-3 s-1 by simply dividing by the Avogadro constant.

For one gas only :

The collision density is on interest because it sets an upper limit on the rate with which two gas molecules can react. Actual chemical reaction rates are usually much smaller than the collision rates, indicating that not every collision leads to reaction.

For one gas only :

Collision frequencies z1(1) and collision densities z11 for four gases are given in Table 3.1 at 25oC. The collision densities are expressed in mol L-1 s-1 because it is easier to think about chemical reactions in these units.

Example 3.2

For molecular oxygen at 25o+C, calculate the collision frequency $z_{1(1)}$ and the collision density z11 at a pressure of 1 bar. The collision diameter of oxygen is 0.361 nm or 3.61x10-10m.

$$\bar{u} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{(8)(8.314\ JK^{-1}mol^{-1})(298\ k)}{\pi(32\ x10^{-3}\ kgmol^{-1})}\right] = 444\ m\ s^{-1}$$

The number density is given by

ρ

$$= N / V = PN_A / RT = \frac{(1\ bar)(6.022\ x10^{23})(10^{3}\ Lm^{-3})}{(0.083145\ L\ bar\ K^{-1}\ mol^{-1})(298\ K)} = 2.43\ x\,10^{25}\ m^{-3}$$

Example 3.2

The collision frequency is given by

Z1(1)=√2 ρπd2ū

=(1.414)(2.43x1025m-3)π(3.610m)2(444ms-1)

= 6.24 x 109 s-1

Z1(1)=1.26x108 mol L-1 s-1

Mean Free Path

- The mean free path λ is the average distance traveled between collisions.
- It can be computed by dividing the average distance traveled per unit time by the collision frequency.
- For a molecule moving through like molecules.

$$\lambda = \frac{\overline{u}}{z_{1(1)}} = \frac{1}{2^{1/2} \rho \pi d^2}$$

Mean Free Path

Assuming that the collision diameter d is independent to temperature,

the temperature and pressure dependence of the mean free path may be obtained by substituting the ideal gas law in the form $\rho = P/kT$:

$$\lambda = \frac{1}{2^{1/2} \pi d^2}$$

Thus, at constant temperature, the mean free path is inversely proportional to the pressure.

Mean Free Path

The collision density is given by

$$z_{11} = \frac{1}{2^{1/2}} \rho^2 \pi d^2 \bar{u}$$

$$= (0.707)(2.43\text{x}10^{25}\,\text{m}^{-3})^2 \pi (3.61\text{x}10^{-10}\,\text{m})^2 (444\,\text{m s}^{-1})$$

$$= 7.58\text{x}10^{34}\,\text{m}^{-3}\text{s}^{-1} = \frac{(7.58\text{x}10^{34}\,\text{m}^{-3}\text{s}^{-1})(10^{-3}\,\text{m}^3\text{L}^{-1})}{6.022\text{x}10^{23}\,\text{mol}^{-1}}$$

Z11= 1.26x10^{8} mol L^{-1} s^{-1}

Example 3.3

For oxygen at 25oC the collision diameter is 0.361 nm. What is the mean free path at (a) bar pressure, and (b) 0.1 Pa pressure?

(a) Since from example 3.2, $\rho = 2.43\text{x}10^{25}\ \text{m}^{-3}$

$$\lambda = \frac{\mathbf{1}}{\mathbf{2}^{1/2}\rho\pi\,\mathbf{d}^{2}}$$

$$\lambda = [(1.414)(2.43\text{x}10^{25}\text{m}^{-3})\pi(3.61\text{x}10^{-10}\text{m})^2]^{-1} = 7.11\text{x}10^{-8}\text{m}$$

Example 3.3

(b) $$\rho = \frac{PN_A}{RT} = \frac{(0.2\ \mathrm{Pa})(6.022\ \mathrm{x}\,10^{23}\ \mathrm{m}^{-1})}{(8.314\ \mathrm{J\ K^{-1}\,mol^{-1}})(298\ \mathrm{K})} = 2.43\ \mathrm{x}\,10^{19}\ \mathrm{m}^{-3}$$

$$\lambda = [(1.414)(3.14)(3.61\mathrm{x}10^{-10}\ \mathrm{m})^2(3.43\mathrm{x}10^{19}\ \mathrm{m}^{-3})]^{-1}$$

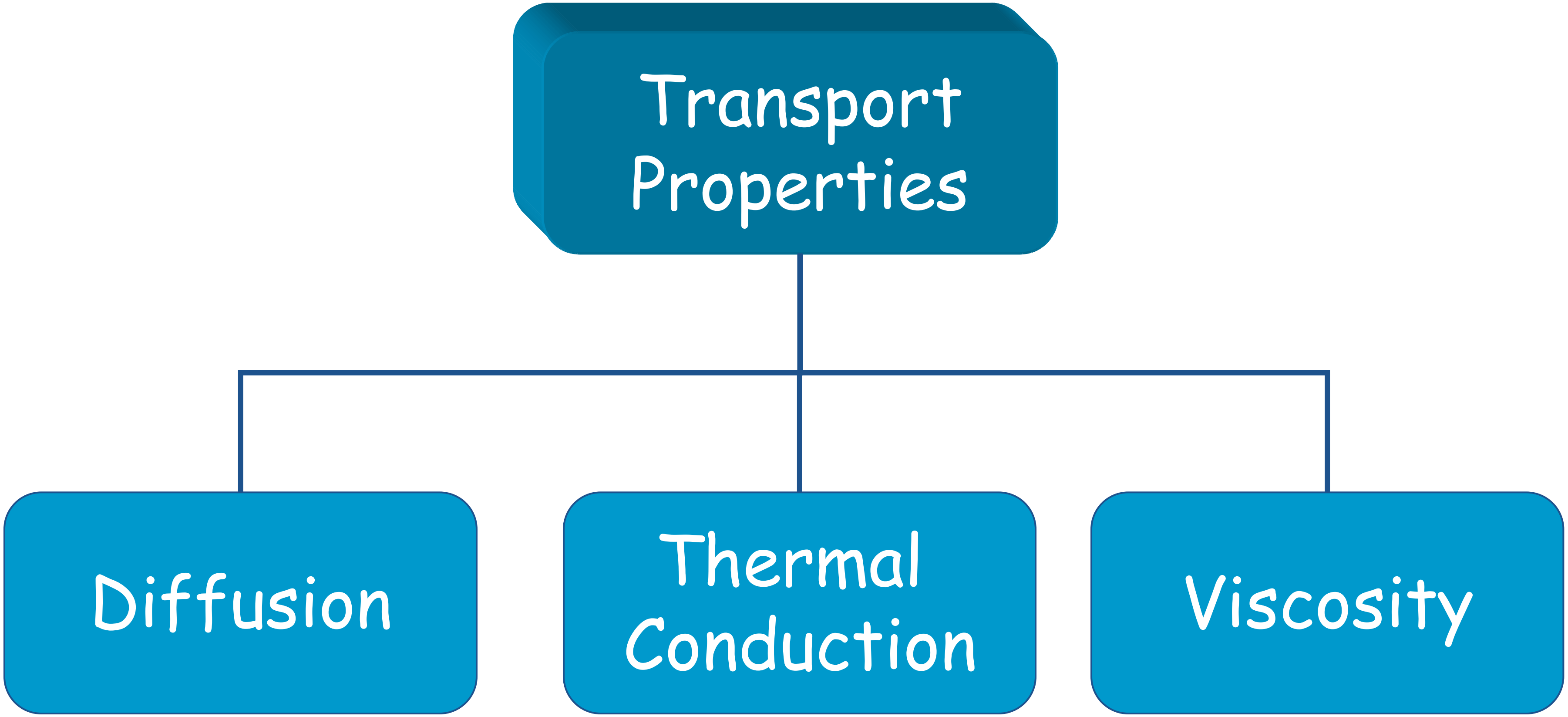
$= 0.071$ m = 7.1 cm

At pressure so low that the mean free path becomes comparable with the dimensions of the containing vessel, the flow properties of the gas become markedly different from those at higher pressures.

Theory of Gases

- Kinetic Theory of Gases
- Equations of Real Gases
- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases

TRANSPORT PHENOMENA IN GASES



Transport Properties

Diffusion

Thermal Conduction

Viscosity

TRANSPORT PHENOMENA IN GASES

If a gas is not uniform with respect to

- Composition
- temperature, and
- velocity,

transport processes occur until the gas becomes uniform.

<u>Examples:</u>

(1) Open a bottle of perfume at the front of a classroom:

Good smell moves from front row to rear (Diffusion).

(2) Metal bar, one end hot and one end cold:

Heat flows from hot to cold end until temperature becomes (Thermal Conduction)

TRANSORT PROPERTIES

TRANSPORT PROPERTIES OF GASES

DIFFUSION

Transport of (labelled) particles

THERMAL CONDUCTION

Transport of thermal energy

VISCOSITY

Transport of momentum in one direction through a gas in another direction

TRANSPORT PHENOMENA IN GASES

In each case,

- Rate of flow ∞ Rate of change of some property with distance, a so-called **gradient**
- All have same mathematical form:

  Flow of_____(per unit area, unit time) = (____x gradient____)

Diffusion: Fick's Law

(matter) (diffusion coefficient) (concentration)

J_{iz} $-D$ $\frac{dc_i}{dz}$

The flux of component i in the z direction due to diffusion is proportional to the concentration gradient dci/dz, according to Fick's law:

$$J_{iz} = -D\frac{dc_i}{dz} \tag{6.1}$$

Diffusion: Fick’s Law

J_{iz} is the flux and

*Expressed in terms of quantity per unit area per unit time.

* J_{iz} has the units mol m^{-2} s^{-1},

* dc_i/dz has the units of mol m^{-4}, and

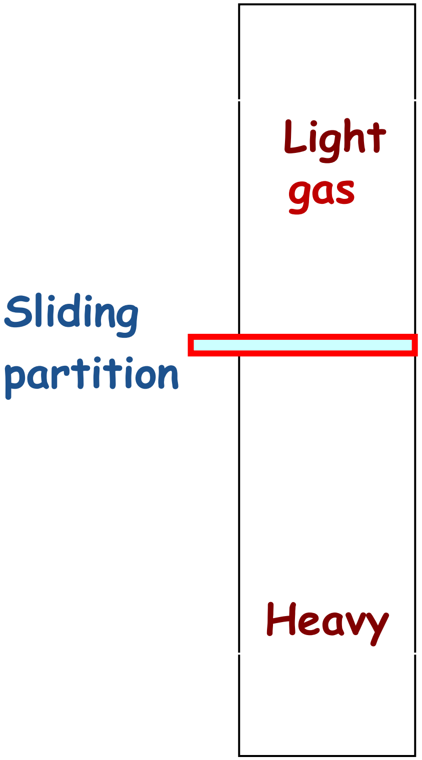
* D has units of m^2 s^{-1}.

Diffusion: Fick’s Law

* The negative sign comes from the fact that if C_i increases in the positive z direction $_{dCi\ /dz}$ is positive, but the flux is in the negative z direction because the flow is in the direction of lower concentrations

Determination of D for the diffusion of one gas into another

- The sliding partition is withdrawn for a definite interval of time.
- From the average composition of one chamber or the other, After a time interval, D may be calculated.



Thermal Conduction: Fourier's Law

Transport of heat is due to a gradient in temperature.

(heat) (thermal conductivity) (temperature)

q_z $= - K_T$ $\frac{dT}{dz}$

$$\therefore q_z = -K_T \frac{dT}{dz} \qquad (6.2)$$

- K is the thermal conductivity.
- q_z has the units of J m^{-2} s^{-1} and
- d_T/d_z has the units of K m^{-1},
- K_T has the units of J m^{-1} s^{-1} K^{-1}.
- The negative sign indicates that if d_T/d_z is positive, the flow of heat is in the negative z direction, which is the direction toward lower temperature.

Thermal Conduction: Fourier’s Law

Viscosity: is a measure of the resistance that a fluid offers to an applied shearing force.

- Consider what happens to the fluid between parallel planes
- when the top plane is moved in the y direction at a constant speed relative to the bottom plane while maintaining a constant distance between the planes (coordinate z)

Thermal Conduction: Fourier’s Law

- The planes are considered to be very large, so that edge effects may be ignored.

- The layer of fluid immediately adjacent to the moving plane moves with the velocity of this plane.

- The layer next to the stationary plane is stationary; in between the velocity usually changes linearly with distance,.

Thermal Conduction: Fourier’s Law

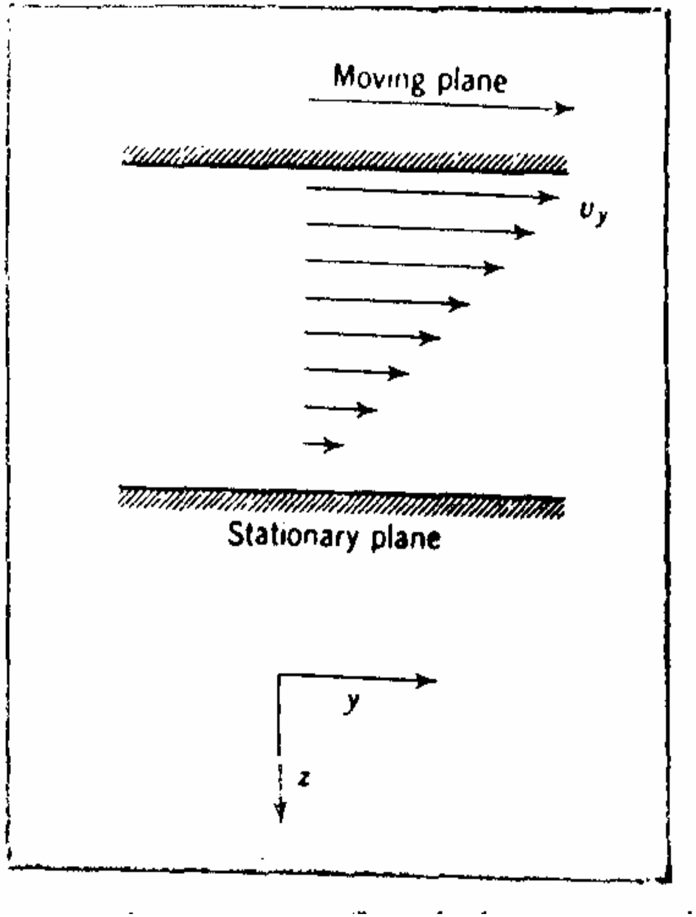
The velocity gradient

Rate of change of velocity with respect to distance measured perpendicular to the direction of flow is represented by

du_y/ dz

The viscosity η is defined by the equation

$$F = -\eta \frac{du_y}{dz} \qquad (6.3)$$

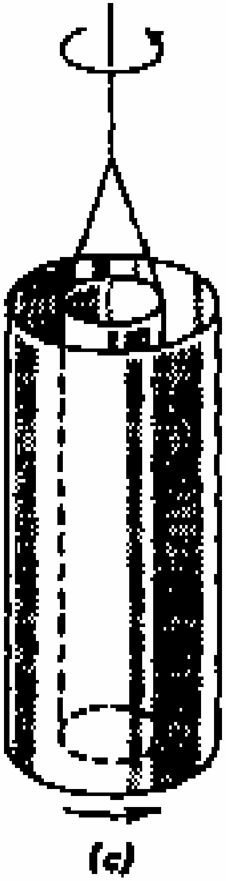


Thermal Conduction: Fourier’s Law

- F is the force per unit area required to move one plane relative to the other.
- The negative sign comes from the fact that if F is in the +y direction, the velocity u_y decreases in successive layers away from the moving plane and du_y/dz is negative.

Thermal Conduction: Fourier's Law

- The thermal conductivity is determined by the hot wire method
- Determination of the rate of flow through a tube, the torque on a disk that is rotated in the fluid, or other experimental arrangement.
- The outer cylinder is rotated at a constant velocity by an electric motor.



Thermal Conduction: Fourier’s Law

- Since 1N = 1 kg m s^{-2}, 1 Pa s = 1 kg m^{-1} s^{-1}. A fluid has a viscosity of 1 Pa s if a force of 1 N is required to move a plane of 1 m^2 at a velocity of 1 m s^{-1} with respect to a plane surface a meter away and parallel with it.

- The cgs unit of viscosity is the poise, that is, 1 $gs^{-1}cm^{-1}$ 0.1 Pa S = 1 poise.

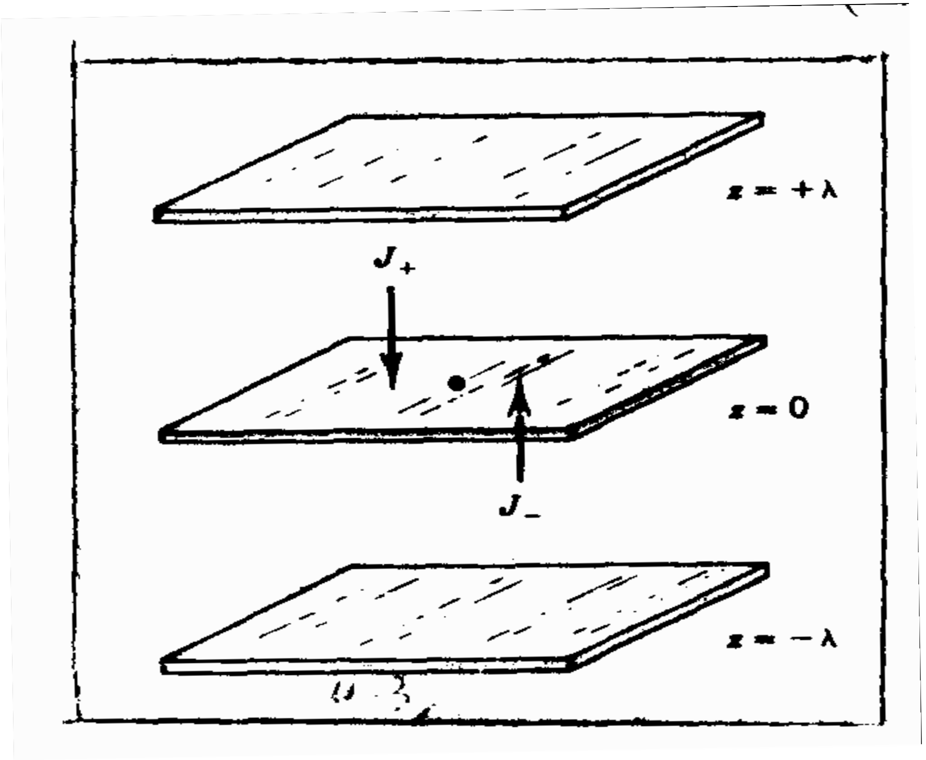
Calculation of Transport Coefficients

To calculate the transport coefficients

D, K_T, and η

even for hard-sphere molecules, needs to consider how the Maxwell-Boltzmann distribution is disturbed by a gradient of concentration, temperature or velocity.

Diffusion Coefficient



Planes constructed at distance ±λ (the mean free path) from the origin. The concentration gradient is in the z direction.

Where ρ_o is the number density of particles in the plane at z = 0.

The density of particles at z = +λ is given by the term in brackets

Diffusion Coefficient

- Consider the diffusion of molecules in a concentration gradient in the z direction and we are at $z = 0$.

- Imagine that we construct planes parallel to the xy plane at $\mathbf{x} = \pm\lambda$, where λ is the mean free path.

- We choose planes at the mean free path because molecules form more distant points will, on average, have suffered collisions before reaching $z = 0$.

Diffusion Coefficient

- Calculate the flux of particles across z = 0 due to the molecules above (z>0) and below **(z<0)**. The flux across **z = 0** from above is

$$J_+ = \left[\rho_0 + \lambda\left(\frac{d\pi}{dz}\right)\right]\frac{\overline{u}}{4}$$

Diffusion Coefficient

Similarly, the flux across z = 0 due to the molecules below z = 0 is

$$J_{-} = \left[\rho_o - \lambda\left(\frac{d\rho}{dz}\right)\right]\frac{\bar{u}}{4}$$

The net flux of particles across the plane z = 0 is then

$$J = -\frac{1}{2}(\bar{u})\frac{d\rho}{dz}$$

This equation can be compared with Eq. 5.1 to obtain

$$D_a = \frac{1}{2}(u)\lambda = \left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\rho\pi d^2}$$

Diffusion Coefficient

- where the subscript 'a' indicates approximate value.
- The exact theoretical expression for the diffusion coefficient of hard spheres is:

$$D = \frac{3\pi}{8}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\rho\pi d^{2}} = \frac{3}{8}\left(\frac{RT}{\pi M}\right)^{1/2}\frac{1}{\rho d^{2}}$$

Example 6.1

Predict $D_{(O2,N2)}$ of an equimolar mixture of O_2 and N_2 gases at 1.00 atm and 0^0C using d_{O2} = 0.353 nm and d_{N2} = 0.373 nm.

$$\rho = \frac{N}{V} = \frac{nN_A}{V} = \frac{N_A P}{RT} \qquad \therefore \rho = \frac{(101.325\ \mathrm{Pa})(6.022\mathrm{x}\ 10^{23}\, mol^{-1})}{(8.314\ \mathrm{m}^3 PaK^{-1} mol^{-1})(273K)} = 2.69x10^{25} m^{-3}$$

$$d_{(O_2,N_2)} = (0.353\ \mathrm{nm} + 0.373\ \mathrm{nm})/2 = 0.363\ \mathrm{nm}$$

$$d_{(O_2,N_2)} = \frac{3}{8}\left[\frac{(0.314\ \ \mathrm{JK}^{-1} mol^{-1})(273\ \ \mathrm{K})}{\pi(32.00\ x10^{-3}\ \ \mathrm{kg\ \ mol}^{-1})}\right]^{1/2}$$

$$x\frac{1}{(3.63x10^{-10}m)^2(2.64x10^{-3}kg\,\mathrm{mol}^{-1})} = 1.59x10^{-5} m^2 s^{-1}$$

Example 6.1

A similar simplified model for thermal conductivity of hard spheres yield the approximate value

$$K_T = \frac{1}{T}\frac{\overline{C}_u}{3N_A}\lambda(u)\rho = \frac{2\overline{C}_u}{3N_A}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\pi d^2}$$

The exact expression for hard sphere is:

$$K_T = \frac{25}{32}\left(\frac{kT}{\mu n}\right)^{1/2}\frac{C_v}{N_A d^2}$$

Example 6.2

Calculate the thermal conductivity coefficient for water vapor at 25°C assuming d = 0.50 nm and

C_v = 25.26 JK^{-1} mol^{-1}.

Substituting data into Eq. (4.11) gives

$$K_T = \frac{25}{32}\left[\frac{(1.381\text{x}10^{-23}\,\text{J.K}^{-1})(298\,\text{K})}{\pi(18.02\text{x}10^{-3}\,\text{kg mol}^{-1})/6.022\text{x}10^{23}\ \text{mol}^{-1})}\right]^{1/2}$$

$$\text{x}\,\frac{25.26\,\text{JK}^{-1}\text{mol}^{-1}}{(6.022\text{x}10^{23}\text{mol})(5.0\text{x}10^{-10}\text{m})^2} = 0.027\,\text{Jm}^{-1}\text{s}^{-1}\text{K}^{-1}$$

Example 6.2

Finally, the approximate model for the viscosity of hard spheres yields:

$$\eta_a = \frac{1}{3}\rho\langle u\rangle m\lambda = \frac{2}{3}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{\pi d^2}$$

whereas the exact expression for hard spheres is

$$\eta = \frac{3}{32\sqrt{2}}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{d^2}$$

Example 2

Note that this does not imply that real molecules are hard spheres; in fact, we are forcing a model on the experiment. Nevertheless, the results in Table 6.1 show that a consistent set of molecular diameters result from this analysis of the data.

Example 6.3

Calculate the viscosity of molecular oxygen at 273.2K and 1 bar. The molecular diameter is 0.360 nm.

Using the exact equation for hard spheres, we find:

$$m = \frac{32.00 \times 10^{-3}\ \text{kg mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}}$$

$$= 5.314 \times 10^{-26}\ \text{kg}$$

$$\eta = \frac{5\pi}{16}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{\pi d^2}$$

Example 3

$$= \frac{5\pi}{16}\left[\frac{(1.380\text{x}10^{-23}\text{JK}^{-1}(273.2\text{K})}{\pi(5.314\text{x}10^{-26}\text{kg})}\right]^{1/2}\frac{5.314\text{x}10^{-26}\text{kg}}{\pi(0.360\text{x}10^{-9}\text{m})^2}$$

= 1.926 x 10-5 kg m^{-1} s^{-1}