Thermodynamics Lecture Series

Reference: Chap 20 Halliday & Resnick Fundamental of Physics 6th edition

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Kinetic Theory of Gases – Microscopic Thermodynamics

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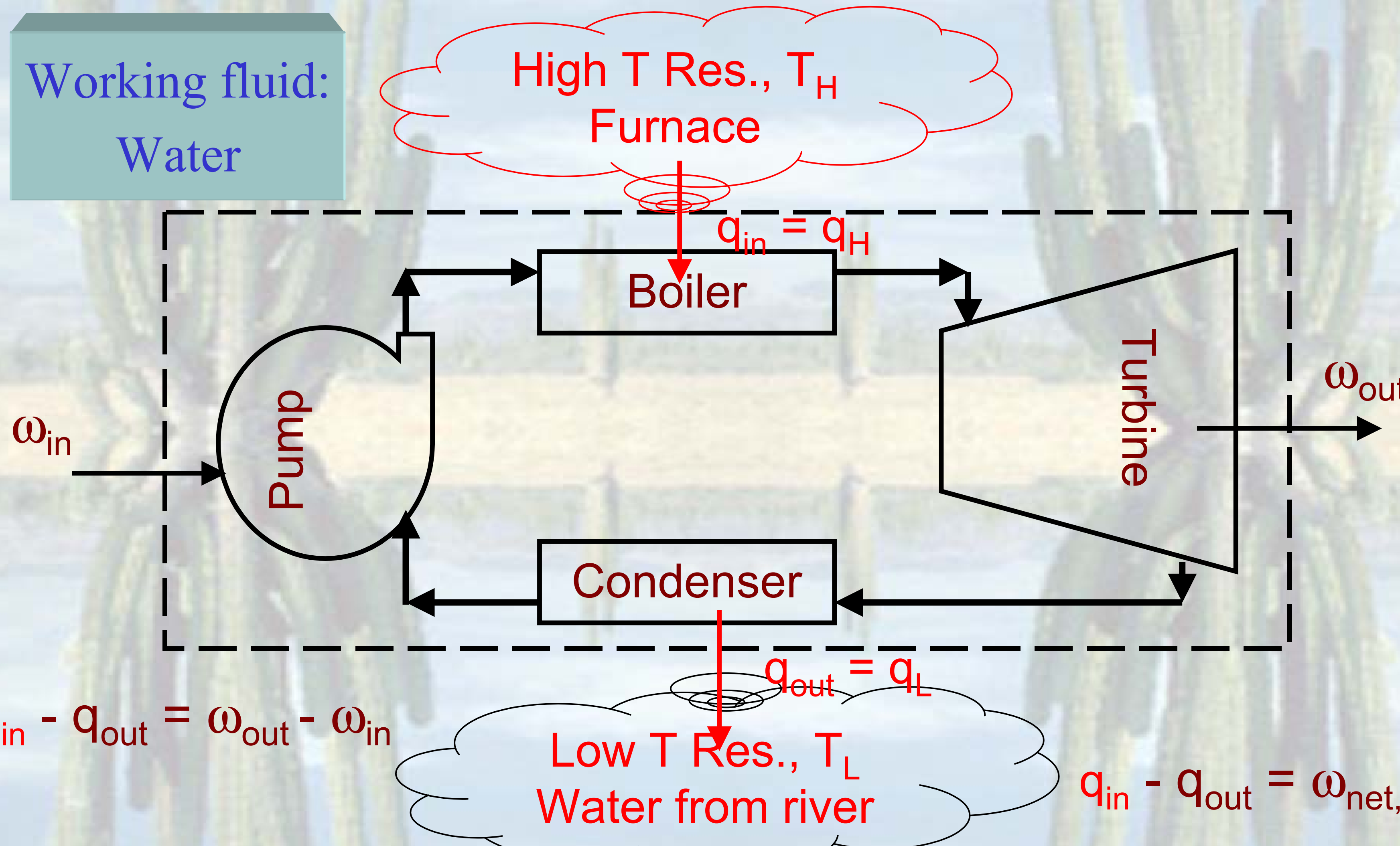
Review – Steam Power Plant

Working fluid: Water



$q_{in} - q_{out} = \omega_{out} - \omega_{in}$

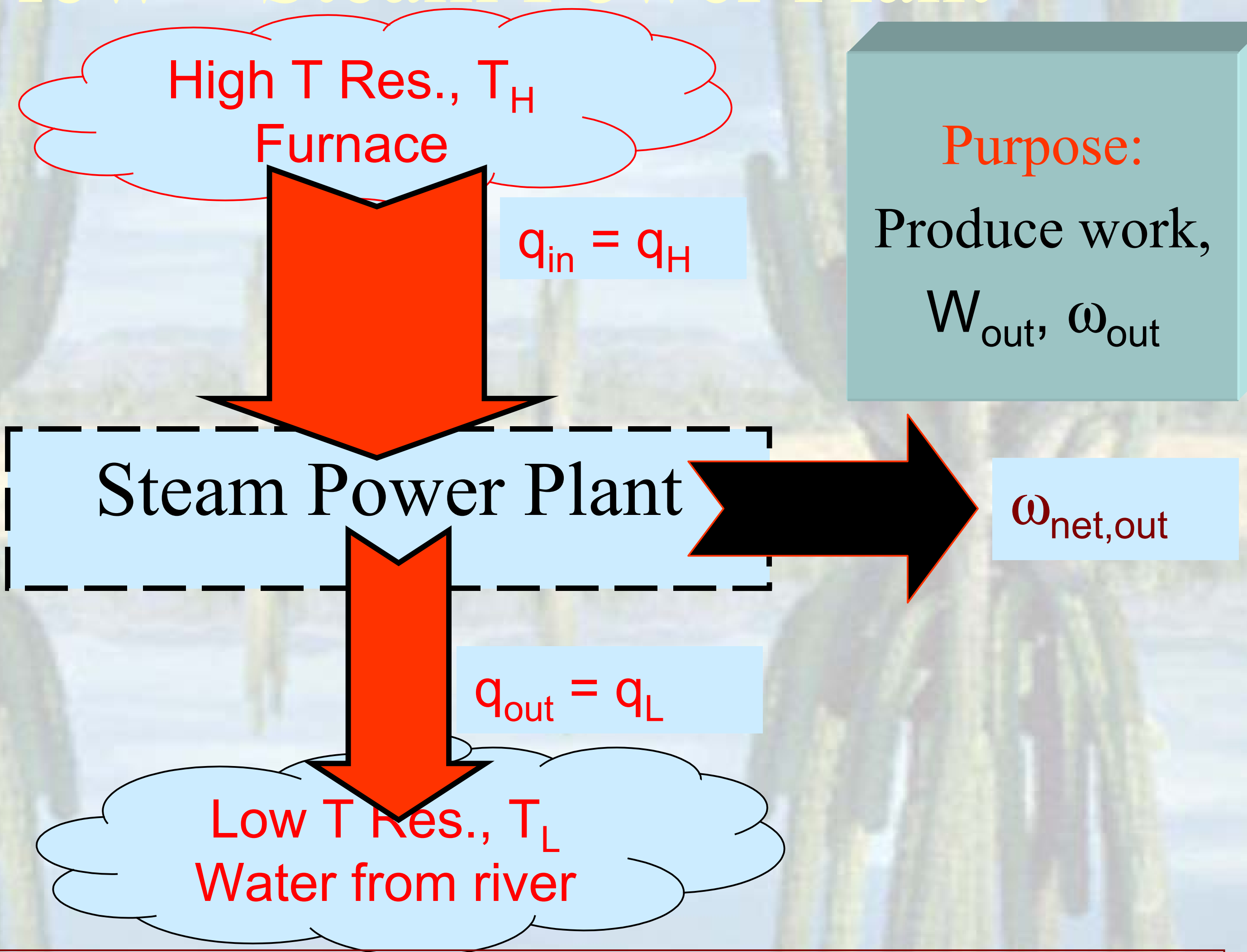
$q_{in} - q_{out} = \omega_{net,out}$

A Schematic diagram for a Steam Power Plant

Review - Steam Power Plant

Working fluid:
Water

Purpose:
Produce work, W_{out}, ω_{out}



An Energy-Flow diagram for a SPP

Review - Steam Power Plant

Thermal Efficiency for steam power plants

$$\eta = \frac{desired \ \ output}{required \ \ input} = \frac{\omega_{net,out}}{q_{in}}$$

$$\eta = \frac{\omega_{net,out}}{q_{in}} = \frac{q_{in} - q_{out}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{q_L}{q_H}$$

$$\eta_{rev} = 1 - \frac{T_L}{T_H}$$

For real engines, need to find q_L and q_H.

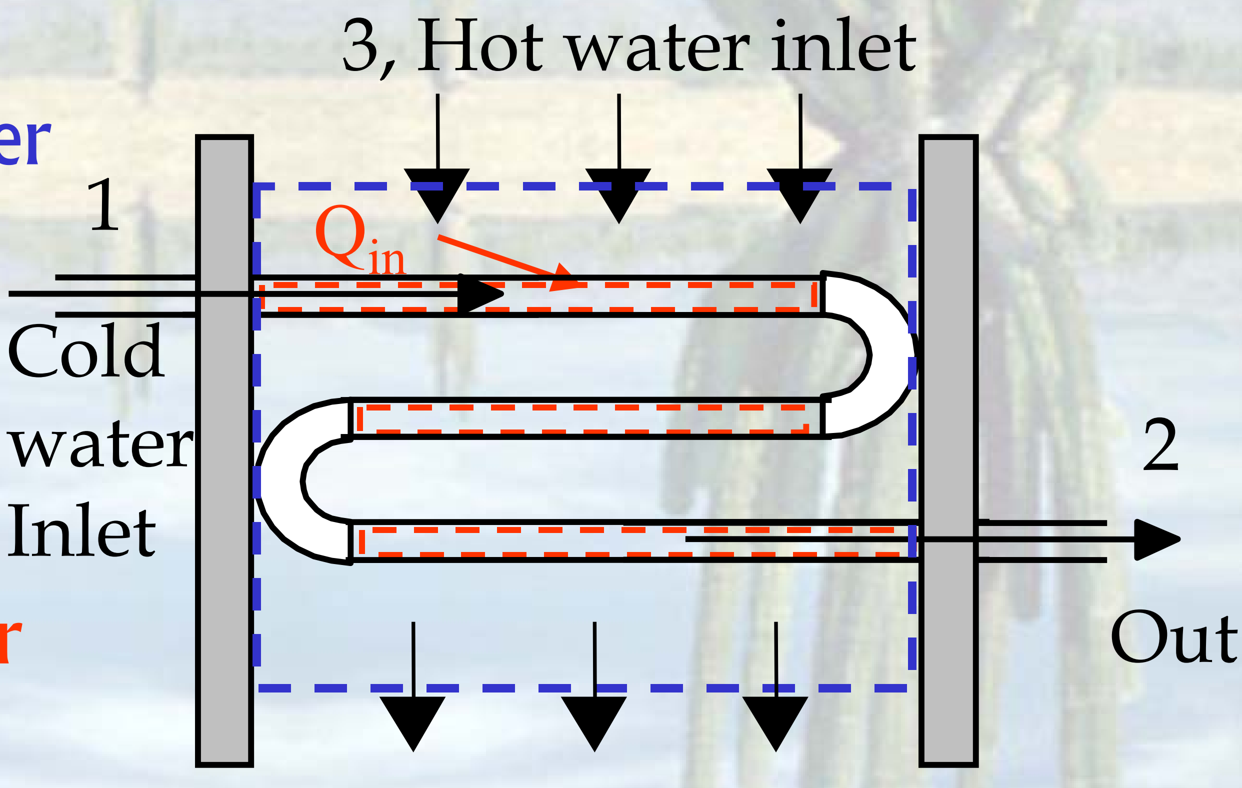
Review - Entropy Balance

Entropy Balance –Steady-flow device

Heat exchanger

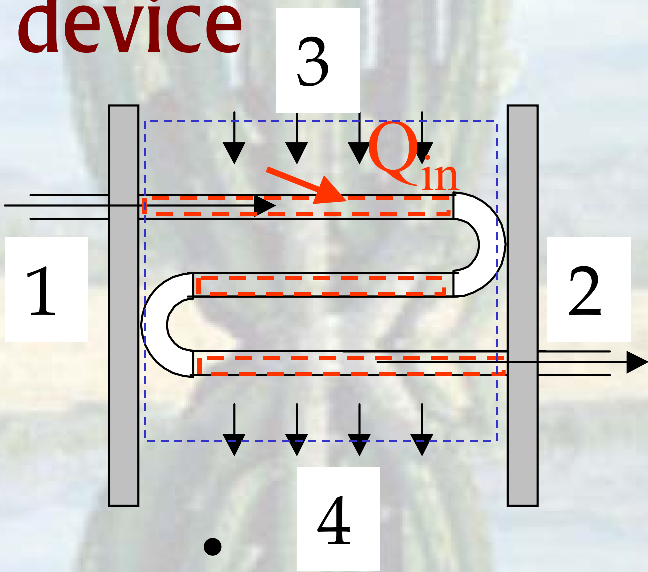
Case 1 – blue border

Case 2 – red border



Review - Entropy Balance

Entropy Balance –Steady-flow device



Heat exchanger: energy balance;

where $\dot{m}_4 = \dot{m}_3 \quad \dot{m}_2 = \dot{m}_1$

Assume $\Delta ke_{mass} = 0, \Delta pe_{mass} = 0$

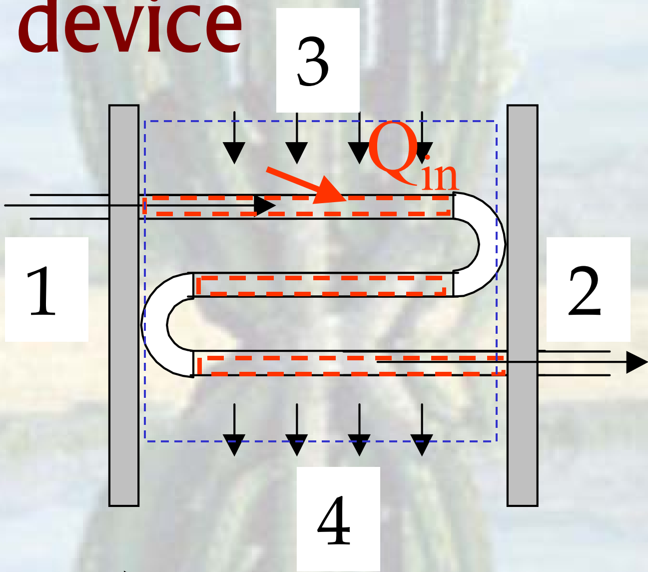
Case 1 $\dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{in} - \dot{W}_{out} = (\dot{m}\vartheta)_{exit} - (\dot{m}\vartheta)_{inlet}$, kW

$$0 = \dot{m}_4 h_4 - \dot{m}_3 h_3 + \dot{m}_2 h_2 - \dot{m}_1 h_1, kW$$

$$\dot{m}_4 (h_4 - h_3) = \dot{m}_2 (h_1 - h_2), kW$$

Review - Entropy Balance

Entropy Balance –Steady-flow device



Heat exchanger: energy balance;

where $\dot{m}_4 = \dot{m}_3 \quad \dot{m}_2 = \dot{m}_1$

Assume $\Delta ke_{mass} = 0, \Delta pe_{mass} = 0$

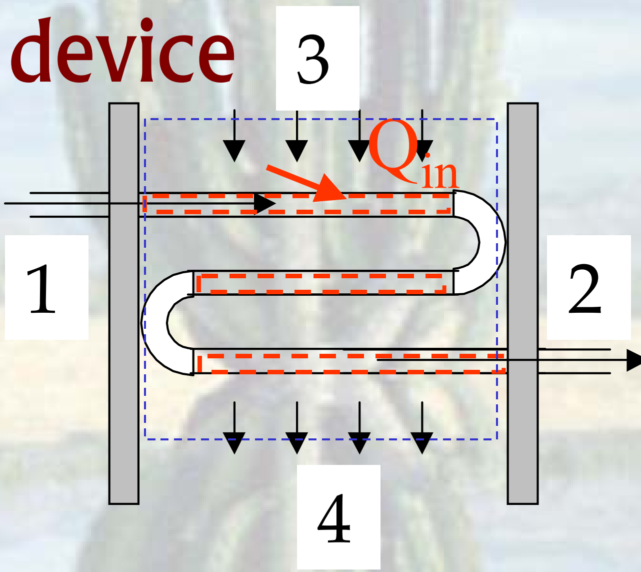
Case 1 $\dot{m}_4 (h_4 - h_3) = \dot{m}_2 (h_1 - h_2)$, kW

Case 2 $\dot{Q}_{in} - \dot{Q}_{out} = \dot{m}_2 \theta_2 - \dot{m}_1 \theta_1$, kW

$$\dot{Q}_{in} - 0 = \dot{m}_2 (h_2 - h_1), kW$$

Review - Entropy Balance

Entropy Balance –Steady-flow device



Heat exchanger:

Entropy Balance

where $\dot{m}_4 = \dot{m}_3 \quad \dot{m}_2 = \dot{m}_1$

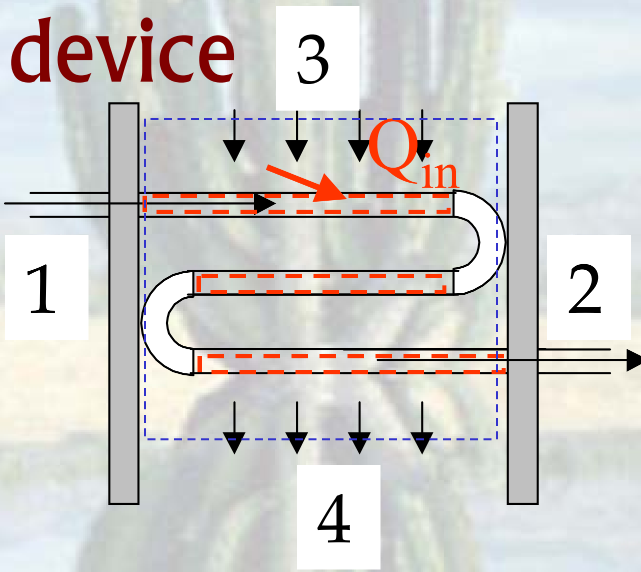
Case 1

$$\dot{S}_{gen} = 0 - 0 + \dot{m}_4 s_4 - \dot{m}_3 s_3 + \dot{m}_2 s_2 - \dot{m}_1 s_1, \quad \frac{kW}{K}$$

$$\dot{S}_{gen} = \dot{m}_4 (s_4 - s_3) + \dot{m}_2 (s_2 - s_1), \quad \frac{kW}{K}$$

Review - Entropy Balance

Entropy Balance –Steady-flow device



Heat exchanger:

Entropy Balance

where $\dot{m}_4 = \dot{m}_3 \quad \dot{m}_2 = \dot{m}_1$

Case 2

$$\dot{S}_{gen} = \frac{\dot{Q}_{out}}{T_{out}} - \frac{\dot{Q}_{in}}{T_{in}} + \dot{m}_2 s_2 - \dot{m}_1 s_1, \quad \frac{kW}{K}$$

$$\dot{S}_{gen} = 0 - \frac{\dot{Q}_{in}}{T_{in}} + \dot{m}_2 (s_2 - s_1), \quad \frac{kW}{K}$$

Introduction - Objectives

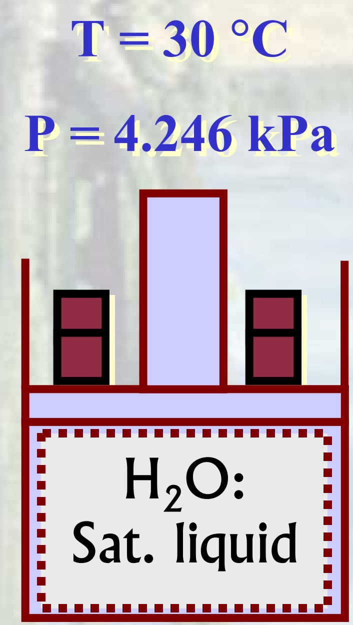
Objectives:

1. *State terminologies and their relations among each other for ideal gases.*
2. *Write the ideal gas equation in terms of the universal gas constant and in terms the Boltzmann constant.*
3. *Derive and obtain the relationship between pressure and root mean square speed of molecules.*
4. *Obtain the relationship of rms speed and gas temperature*

New Way of Looking at Gases

Microscopic Variables

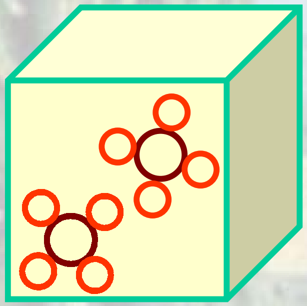
- Classical Thermodynamics
  - Properties are macroscopic measurables: P,V,T,U
  - No inclusion of atomic behaviour
  - Did not discuss about the origin of P,T or explain V.



New Way of Looking at Gases

Microscopic Variables-Molecular Approach

- Kinetic Theory of Gases
  - Pressure exerted by gas related to molecules colliding with walls
  - T and U related to kinetic energies of molecules
  - V filled by gas relate to freedom of motion of molecules.
- Must look at same number of molecules when measure size of samples

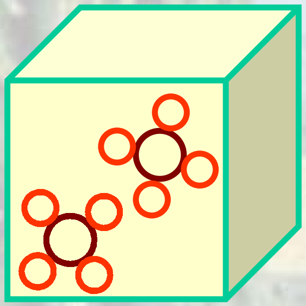


High density

New Way of Looking at Gases

Microscopic Variables-Molecular Approach

- Kinetic Theory of Gases: Sizes
  - Mole: the number of atoms contained in 12 g sample of carbon-12
  - Avogadro's number:
    - $N_A = 6.02 \times 10^{23}$ atoms/mol
  - Number of moles is
    - n is the ratio of number of molecules with respect to N_A

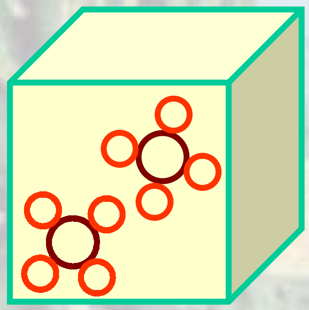


$$n = \frac{N}{N_A}$$

New Way of Looking at Gases

Microscopic Variables-Molecular Approach

- Kinetic Theory of Gases: Sizes
  - Number of moles is
    - n is the ratio of sample mass to the molar mass, M or molecular mass m



High density

$$n = \frac{N}{N_A} = \frac{M_{sample}}{M} = \frac{M_{sample}}{mN_A}$$

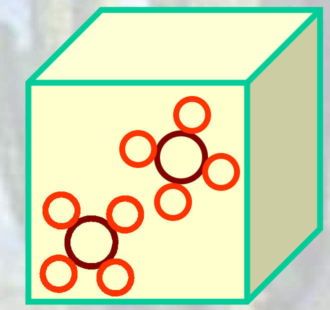
- Where the molar mass is related to the molecular mass by Avogadro number

$$M = mN_A$$

New Way of Looking at Gases

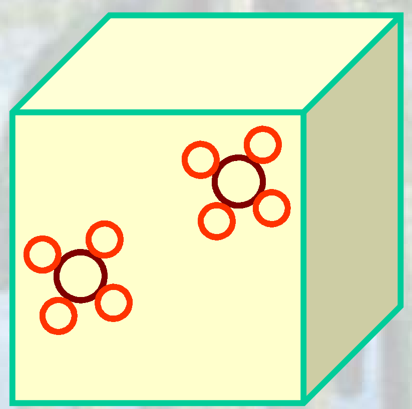
Ideal Gases

- Low density (mass in 1 m^3) gases.
  - Molecules are further apart



High density

- Real gases satisfying condition $P_{gas} << P_{crit}$; $T_{gas} >> T_{crit}$, have low density and can be treated as ideal gases



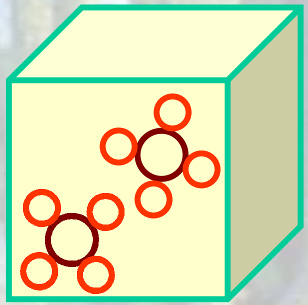
Low density Molecules far apart

New Way of Looking at Gases

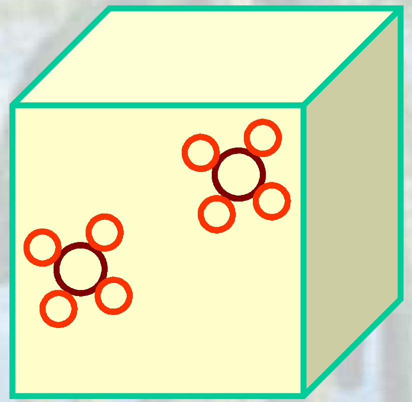
Ideal Gases

➢ **Equation of State** - P-ν-T behaviour

$P\nu = RT$ (energy contained by 1 kg mass) where ν is the specific volume in m^3/kg, R is gas constant, $\mathrm{kJ/kg{\circ}K}$, T is absolute temp in Kelvin.



High density



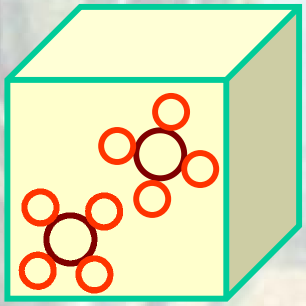
Low density

Molecules far apart

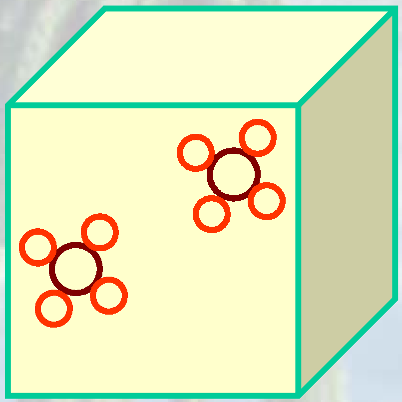
New Way of Looking at Gases

Ideal Gases

- **Equation of State** - P-ν-T behaviour
  - $P\nu = RT$, since $\nu = V/M_{sam}$ then, $P(V/M_{sam}) = RT$. So, $PV = M_{sam}RT$, in $kPa \cdot m^3 = kJ$.
  - Total energy of a system.



High density

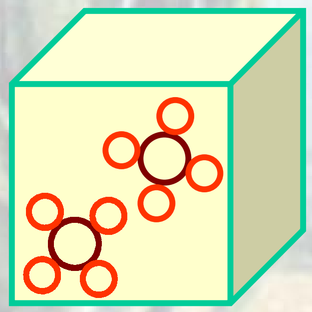


Low density

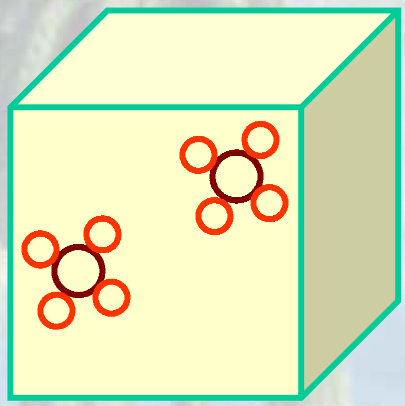
New Way of Looking at Gases

Ideal Gases

- **Equation of State** - P-ν-T behaviour
  - $PV = M_{sam}RT = nMRT = n(MR)T$
    But $R_u = MR$. Hence, can also write $PV = nR_uT$ where
  - n is no of kilomoles, kmol,
  - M is molar mass in kg/kmole ,
  - R is a gas constant and
  - R_u is universal gas constant;
    $R_u = MR = 8.314$ kJ/kmol.K



High density

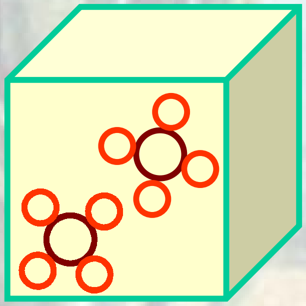


Low density

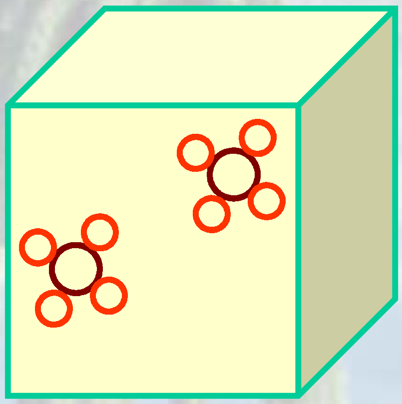
New Way of Looking at Gases

Ideal Gases

- **Equation of State** - P-ν-T behaviour
  - $PV = nR_uT$ $= nkN_AT = (N/N_A)(kN_A)T$. Hence, can also write $PV = nkT$ where
  - n is no of kilomoles, kmol,
  - N is no of molecules,
  - k is Boltzmann constant; $nR_u = Nk$.
  - $R_u = 8.314$ kJ/kmol.K
  - $k = R_u / N_A = 1.38 \times 10^{-23}$ J/K



High density

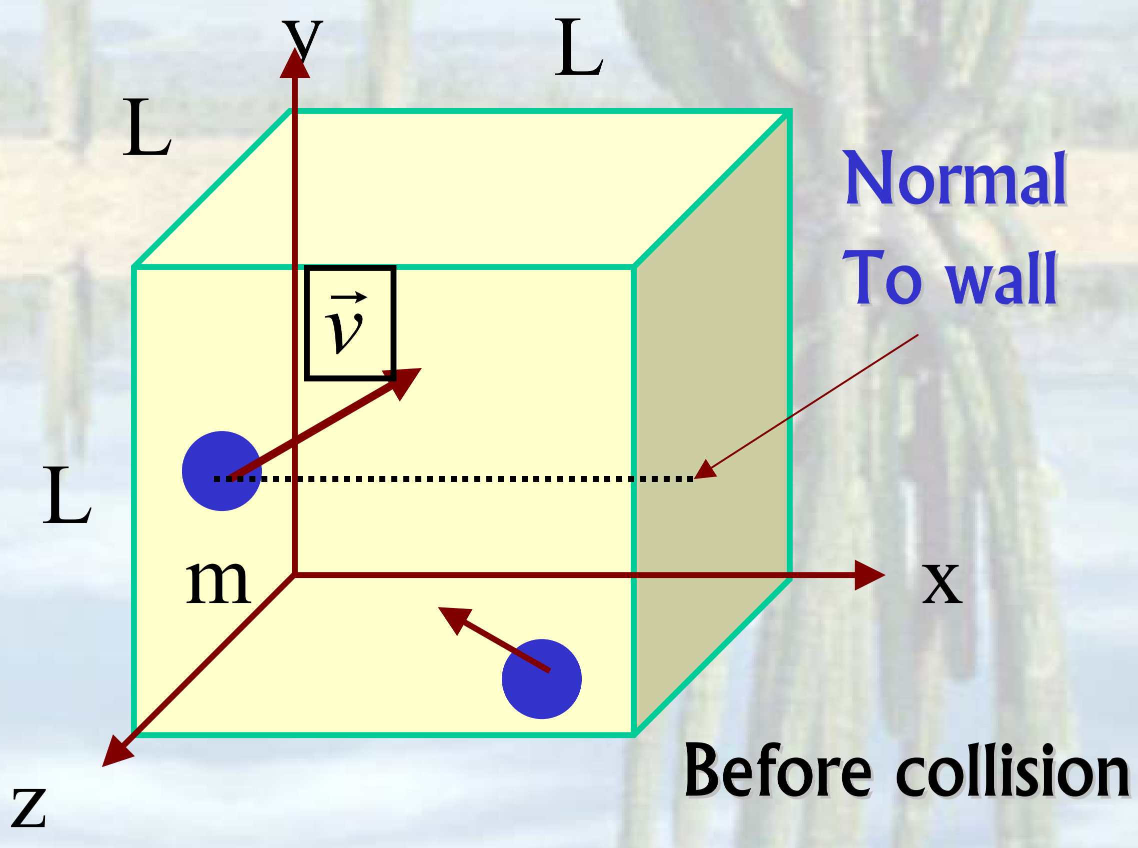


Low density

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- How is the pressure P that an ideal gas of n moles confined to a cubical box of volume V and held at temperature T, related to the speeds of the molecules??



New Way of Looking at Gases

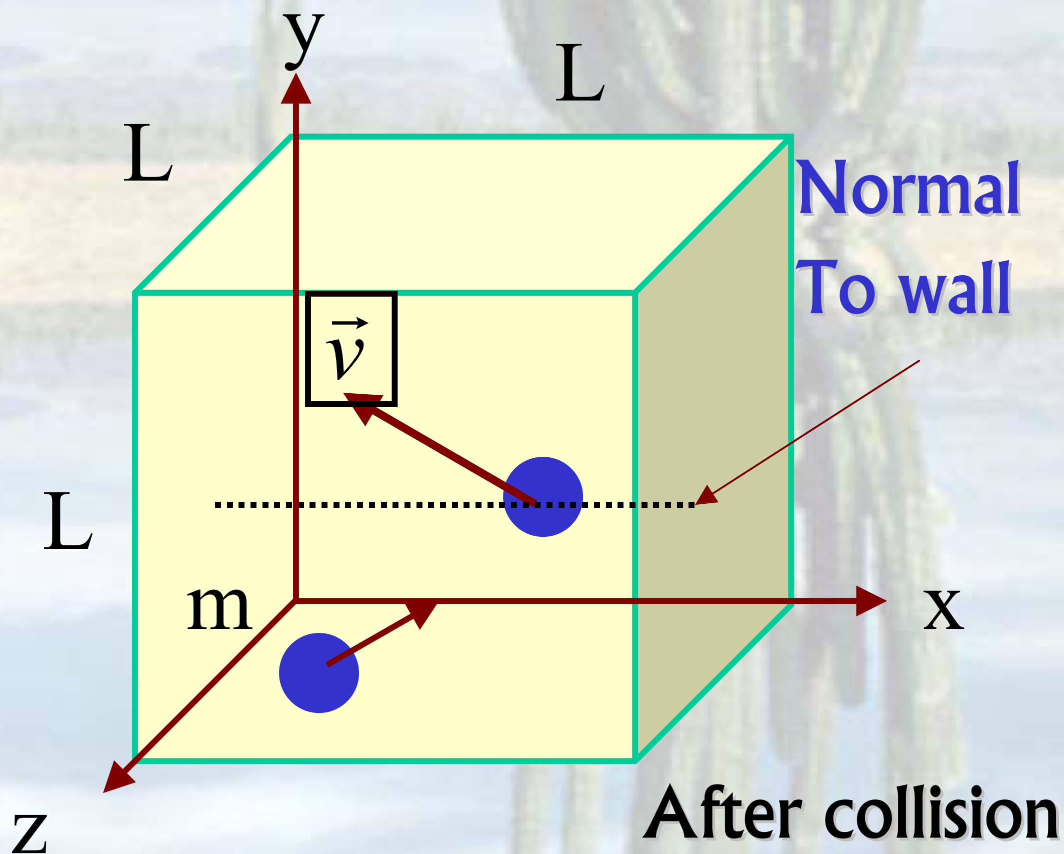
Pressure, Temperature and Root Mean Square Speed

- Assume elastic collision, then after collide with right wall, only x component of velocity will change. Then momentum change is:

$$\Delta p_x = p_f - p_i$$

$$= -mv_x - mv_x$$

$$= -2mv_x$$



New Way of Looking at Gases

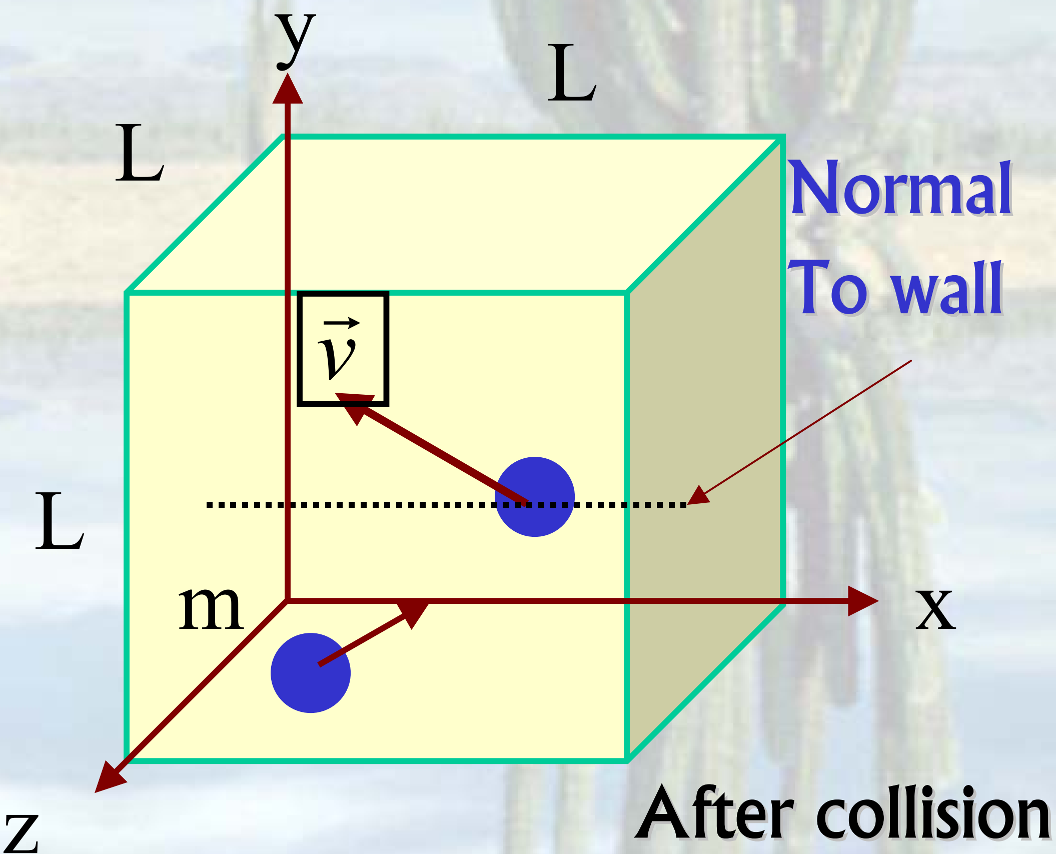
Pressure, Temperature and Root Mean Square Speed

- So momentum change received by the wall is:

$$\Delta p_x = +2mv_x$$

- The time to hit the right wall again is

$$\Delta t = \frac{2L}{v_x}$$



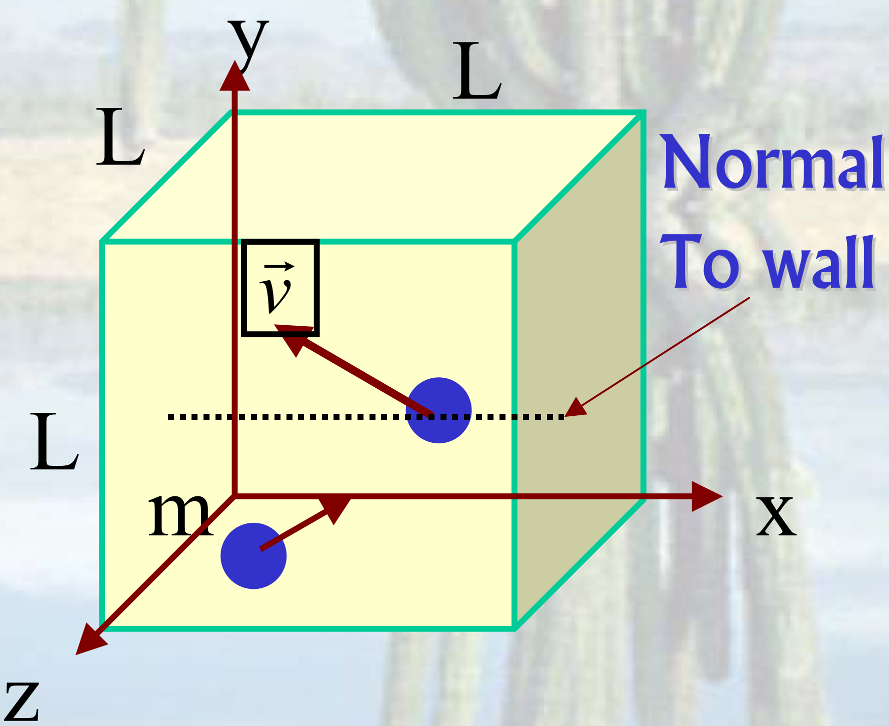
New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- So average rate of momentum transfer received by the wall due to 1 molecule is:

$$\frac{\Delta p_x}{\Delta t} = \frac{+2mv_x}{2L/v_x}$$

$$\frac{\Delta p_x}{\Delta t} = \frac{mv_x^2}{L} = F_x$$

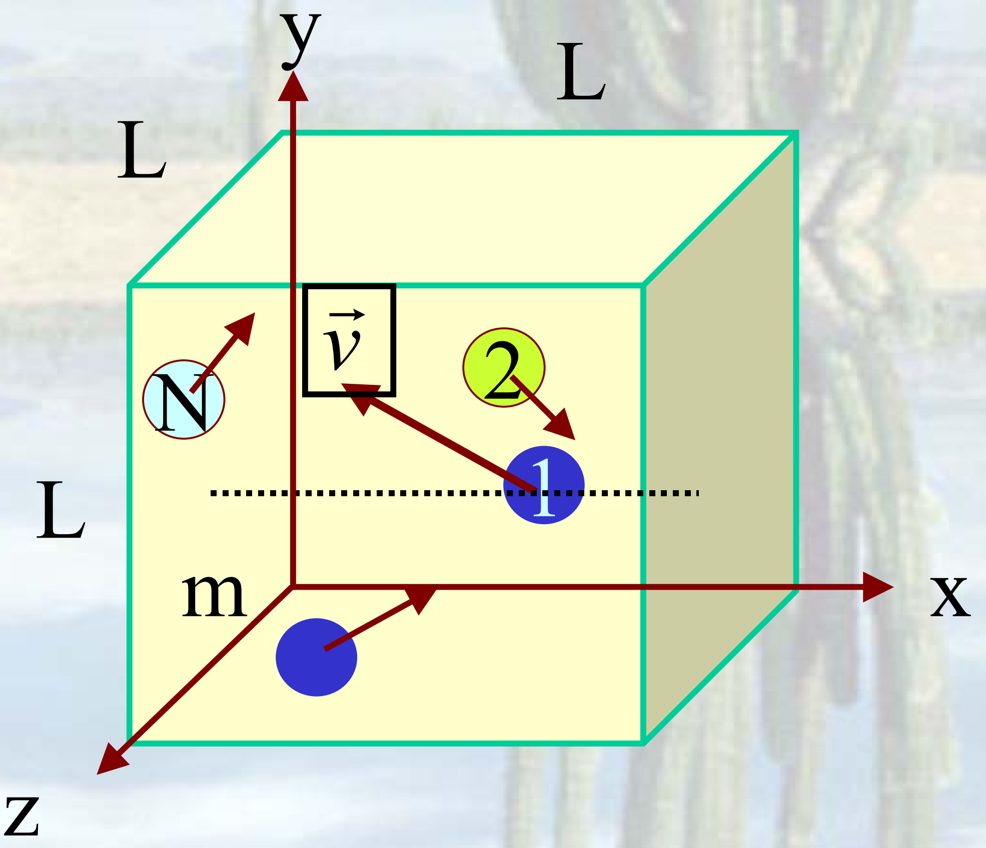


After collision

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- So average rate of momentum transfer received by the wall due to N molecules is:



New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- The total force along x is the sum due to collision by all N molecules with different speeds. The pressure on the wall is the force exerted for each unit area and is then:

$$P = \frac{F_x}{L^2} = \frac{m{v_{x1}}^2/L + m{v_{x2}}^2/L + .. + m{v_{xN}}^2/L}{L^2}$$

$$P = \left(\frac{m}{L^3}\right)\left({v_{x1}}^2 + {v_{x2}}^2 + .. + {v_{xN}}^2\right)$$

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- The total force along x is the sum due to collision by all N molecules with different speeds. The pressure on the wall is then:

$$P = \left(\frac{m}{L^3}\right)\left(v_{x1}^{\;2} + v_{x2}^{\;2} + .. + v_{xN}^{\;2}\right)$$

- But there are N velocities representing N molecules and so we can represent the different speeds by an average speed. Note also that $n = N/N_A$. So, $N = nN_A$. Then the pressure on the wall is:

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- But there are N velocities representing N molecules and so we can represent the different speeds by and average speed. Note also that $n = N/N_A$. So, $N = nN_A$. Then the pressure on the wall is:

$$P = \left(\frac{mnN_A}{L^3}\right)\left(v_x^{\,2}\right)_{avg}$$

- But mN_A is the molar mass, M of the gas mass of 1 mol and L^3 is the volume of the box. So,

$$P = \left(\frac{nM}{V}\right)\left(v_x^{\,2}\right)_{avg}$$

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- Then the pressure is:

$$P = \left(\frac{mnN_A}{L^3}\right)\left(v_x^{\ 2}\right)_{avg}$$

$$P = \left(\frac{nM}{V}\right)\left(v_x^{\ 2}\right)_{avg}$$

- But mN_A is the molar mass, M of the gas mass of 1 mol and L^3 is the volume of the box. So,
- In the 3D box each molecule has speed along x,y and z direction.

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

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- Since there are many molecules in the box each moving with different velocities and in random directions, the average square of velocity components are equal.

$$v_x^2 = v_y^2 = v_z^2$$

Then,

$$v^2 = v_x^2 + v_x^2 + v_x^2$$

Hence

$$v_x^2 = \frac{v^2}{3}$$

Finally,

$$P = \left(\frac{nM}{3V}\right)\left(v^2\right)_{avg}$$

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- The square root of the average of the square of the velocity is called root-mean-square speed of the molecules. It means square each speed, find the mean, then take its square root.

$$v_{rms} = \sqrt{\left(v^2\right)_{avg}}$$

So,

$$v_{rms}^{\;\;2} = \left(v^2\right)_{avg}$$

Hence, the pressure is:

$$P = \frac{nMv_{rms}^{\;\;2}}{3V}$$

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

- The square root of the average of the square of the velocity is called root-mean-square speed of the molecules. It means square each speed, find the mean, then take its square root.

$$v_{rms} = \sqrt{\left(v^2\right)_{avg}}$$

So, $$v_{rms}{}^2 = \left(v^2\right)_{avg}$$

Hence, the pressure is:

$$P = \frac{nMv_{rms}{}^2}{3V}$$

The rms speed can be determined If P,T is known. Using $PV = nR_uT$

$$nR_uT = \frac{nMv_{rms}{}^2}{3}$$

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

Since the square of the root mean square of the velocity is:

$$v_{rms}^{\;2} = \frac{3R_uT}{M}$$

- The root mean square is then:

$$v_{rms} = \sqrt{\frac{3R_uT}{M}}$$

New Way of Looking at Gases

Pressure, Temperature and Root Mean Square Speed

Gas (Values taken at T=300K)	Molar mass, M (10^{-3} kg/kmol)	v_{rms}, (m/s)
Hydrogen (H_2)	2.02	1920
Helium (He)	4.0	1370
Water vapor (H_2O)	18.0	645
Nitrogen (N_2)	28.0	517
Oxygen(O_2)	32.0	483
Carbon dioxide (CO_2)	44.0	412
Sulphur Dioxide (SO_2)	64.1	342

New Way of Looking at Gases

Temperature-Translational kinetic Energy

- Consider a molecule in the box which are colliding with other molecules and changes speed after collision. It moves with translational kinetic energy at any instant

$$KE = \frac{mv^2}{2}$$

- But the average translational kinetic energy is over a period of time is:

$$KE_{avg} = \left(\frac{mv^2}{2}\right)_{avg} = \frac{m}{2}\left(v^2\right)_{avg} = \frac{m}{2}v_{rms}^{\ 2}$$

New Way of Looking at Gases

Temperature-Translational kinetic Energy

- Substitute the rms speed in terms of T, then:

$$KE_{avg} == \frac{m3R_uT}{2M} = \frac{\not{m}3R_uT}{2\not{m}N_A} = \frac{3R_uT}{2N_A}$$

- Note that the molar mass $M = mN_A$. Note also that $R_u = kN_A$. Hence the average translational kinetic energy is:

$$KE_{avg} = \frac{3R_uT}{2N_A} = \frac{3}{2}kT$$

Regardless of mass , all ideal gas molecules at temperature T have the same avg. translational KE.