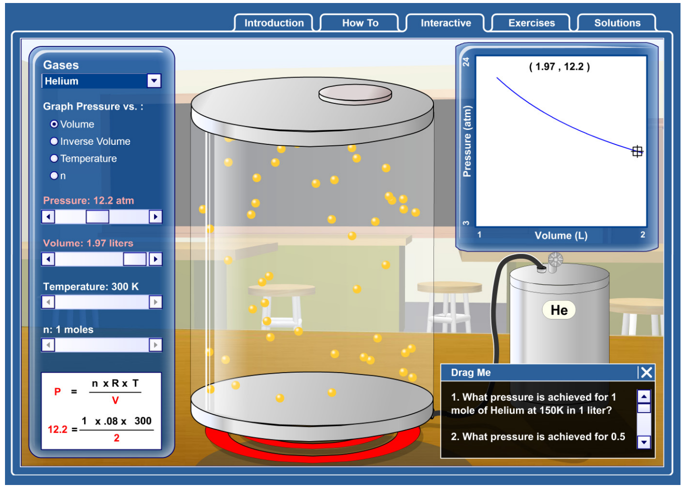
Kinetic Theory of Gases

Physics Enhancement Programme

Dr. M.H. CHAN

Department of Physics, HKBU

Web Resource: Ideal Gas Simulation



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Ideal Gas

- The interatomic forces within the gas are very weak.
- There is no equilibrium separation for the atoms.
  - Thus, no “standard” volume at a given temperature.
- For a gas, the volume is entirely determined by the container holding the gas.
- Equations involving gases will contain the volume, *V*, as a variable
  - This is instead of focusing on ΔV

Ideal Gas Assumptions

- The number of molecules in the gas is large, and the average separation between the molecules is large compared with their dimensions.
  - The molecules occupy a negligible volume within the container.
  - This is consistent with the macroscopic model where we assumed the molecules were point-like.
- The molecules obey Newton’s laws of motion, but as a whole they move randomly.
  - Any molecule can move in any direction with any speed.

Ideal Gas Assumptions

- The molecules interact only by short-range forces during elastic collisions.
  - This is consistent with the macroscopic model, in which the molecules exert no long-range forces on each other .
- The molecules make elastic collisions with the walls.
  - These collisions lead to the macroscopic pressure on the walls of the container.
- The gas under consideration is a pure substance.
  - All molecules are identical.

Notes on Ideal Gas

- An ideal gas is often pictured as consisting of single atoms.
- However, the behavior of molecular gases approximate that of ideal gases quite well.
  - At low pressures.
  - Molecular rotations and vibrations have no effect, on average, on the motions considered.

Gas: Equation of State

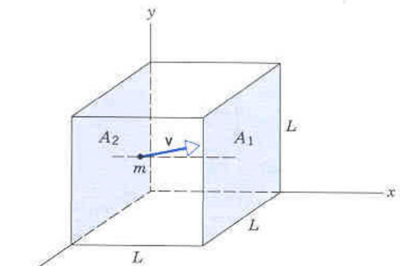
- It is useful to know how the volume, pressure and temperature of the gas of mass m are related.
- The equation that interrelates these quantities is called the equation of state.
  - These are generally quite complicated.
  - If the gas is maintained at a low pressure, the equation of state becomes much easier.
  - This type of a low density gas is commonly referred to as an ideal gas.

Ideal Gas Model

- The ideal gas model can be used to make predictions about the behavior of gases.
  - If the gases are at low pressures, this model adequately describes the behavior of real gases.

The ideal gas model

ideal gas = system of "non-interacting" atoms/molecules.



a single molecule in the box

The Mole

- The amount of gas in a given volume is conveniently expressed in terms of the number of moles.
- One mole of any substance is that amount of the substance that contains Avogadro's number of constituent particles.
  - Avogadro's number $N_A = 6.02 \times 10^{23}$.
  - The constituent particles can be atoms or molecules.

The Mole

- The number of moles can be determined from the mass of the substance: $n = m / M$.
  - M is the molar mass of the substance.
  - Example: Helium, M = 4 g/mol.
  - m is the mass of the sample.
  - n is the number of moles.

Gas Laws

- Boyle's law: When a gas is kept at a constant temperature, its pressure (P) is inversely proportional to its volume (V).

$$PV = \text{Constant.}$$

- Charles law: When a gas is kept at a constant pressure, its volume (V) is directly proportional to its temperature (T).

$$V_1 / T_1 = V_2 / T_2.$$

- Guy-Lussac's law: When the volume of the gas is kept constant, the pressure (P) is directly proportional to the temperature (T).

$$P_1 / T_1 = P_2 / T_2.$$

Ideal Gas Law

- The ideal gas law is the equation of state of a hypothetical ideal gas.
- The equation of state for an ideal gas combines and summarizes the Ideal Gas Law:

$$PV = nRT$$

- R = Universal Gas Constant
  = 8.314 J/mol·K
  = 0.08214 L·atm/mol·K
- Example: Determine the volume of any gas (1 mole, 1 atmospheric pressure, 0^oC)

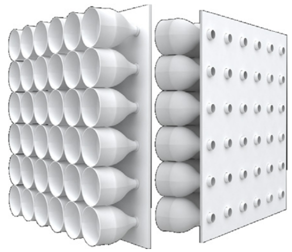
Answer: 22.4 L

Ideal Gas Law

- The ideal gas law is often expressed in terms of the total number of molecules, N, present in the sample.
- $PV = nRT = (N/N_A)\ RT = Nk_BT$
  - k_B = Boltzmann's constant = 1.38×10^{-23} J/K
- It is common to call P, V, and T the thermodynamic variables of an ideal gas.
- If the equation of state is known, one of the variables can always be expressed as some function of the other two.

Application: Eco Cooler

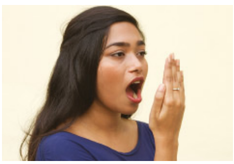
- The Eco-Cooler is a zero electricity air cooler, which made of plastic bottles.
- Helps to reduce temperatures in tin huts to make them bearable to live in.
- Because of the simplicity, everyone is expected to be able to adopt this idea and make their own.



Reference:

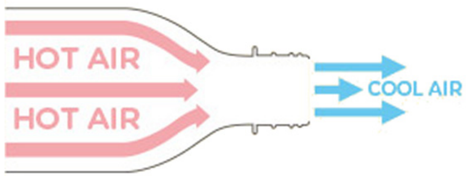
http://revolution-green.com/air-conditioner-less-5/

Application: Eco Cooler



Blow With you mouth wide open.

Blow With you mouth with your lips pursed.



Can you relate this effect to thermodynamics?

Application: Eco Cooler

- The DIY air conditioner has no copyright.
- Instruction manual is available at:

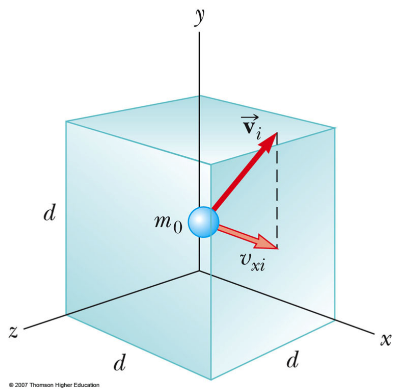
  http://cdn.bigweb.com.bd/eco-cooler/Eco-Cooler.HowToMake.pdf

Molecular Model of an Ideal Gas

- Macroscopic properties of a gas were pressure, volume and temperature.
- Can be related to microscopic description
  - Matter is treated as a collection of molecules.
  - Newton's Laws of Motion can be applied statistically.

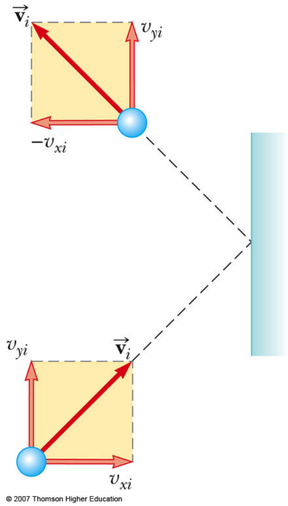
Pressure and Kinetic Energy

- Assume a container is a cube.
  - Edges are length *d*.
- Motion of the molecule: in terms of its velocity components.
- Momentum and the average force.



Pressure and Kinetic Energy

- Assume perfectly elastic collisions with the walls of the container.
- The relationship between the pressure and the molecular kinetic energy comes from momentum and Newton's Laws.



Pressure and Kinetic Energy

- Pressure is proportional to the number of molecules per unit volume (*N*/*V*) and to the average translational kinetic energy of the molecules:

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m_o\overline{v}^2\right)$$

- This equation relates the macroscopic quantity of pressure with a microscopic quantity of the average value of the square of the molecular speed.
- Ways to increase pressure:
  - increase the number of molecules per unit volume; and
  - increase the speed (kinetic energy) of the molecules.

Molecular Interpretation of Temperature

- Temperature is a direct measure of the average molecular kinetic energy:

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m_o\overline{v}^2\right) = Nk_BT \qquad \frac{1}{2}m_o\overline{v}^2 = \frac{3}{2}k_BT$$

<u>Theorem of Equipartition of Energy</u>:
Each translational degree of freedom contributes an equal amount to the energy of the gas

$$\begin{cases} \frac{1}{2}m_o\overline{v}_x^{\,2} = \frac{1}{2}k_BT \\ \frac{1}{2}m_o\overline{v}_y^{\,2} = \frac{1}{2}k_BT \\ \frac{1}{2}m_o\overline{v}_z^{\,2} = \frac{1}{2}k_BT \end{cases}$$

Total Kinetic Energy

- Total Kinetic Energy (translational):

$$K_{\text{Tot}} = N\left(\frac{1}{2}m\overline{v}^2\right) = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$

- If a gas has only translational energy, this is the internal energy of the gas.
- Internal energy of an ideal gas depends only on the temperature.

RMS Speed

Root-Mean-Square Speed of molecules:

$$v_{\text{RMS}} = \sqrt{\frac{3kT}{m_o}} = \sqrt{\frac{3RT}{M}}$$

M = molar mass (in kg per mole) = m_oN_A

Some Root-Mean-Square (rms) Speeds

Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)	Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)
H_2	2.02	1902	NO	30.0	494
He	4.00	1352	O_2	32.0	478
H_2O	18.0	637	CO_2	44.0	408
Ne	20.2	602	SO_2	64.1	338
N_2 or CO	28.0	511			

Quick Quiz

Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A.

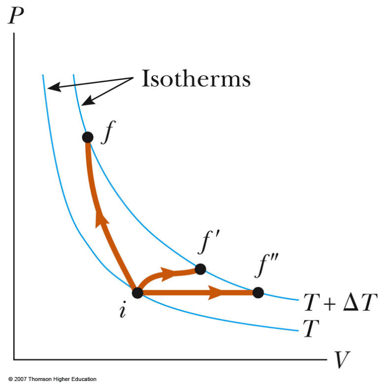
(i) What is the average translational kinetic energy per molecule in container B? [Answer:]

(ii) Describe the internal energy of the gas in container B. [Answer:]

Multiple Choices:
(a) twice that of container A.
(b) the same as that of container A.
(c) half that of container A.
(d) impossible to determine.

Molar Specific Heat

- Consider: An ideal gas undergoes several processes such that change in temperature is ΔT.
- Temperature change can be achieved by various paths (from one isotherm to another).
- ΔT is the same for each process ⇨ ΔE_{int} is also the same.
- Work done on gas (negative area under the curve) is different for each path.



Molar Specific Heat

- From the first law of thermodynamics ($\Delta E_{int} = Q + W$), the heat associated with a particular change in temperature is not unique.
- Specific heats for two processes that frequently occur:
  - Changes with constant pressure
  - Changes with constant volume

Molar Specific Heat

- Constant-volume processes:

$$Q = n\,C_v\,\Delta T \quad \cdots\cdots(1)$$

- Constant-pressure processes:

$$Q = n\,C_p\,\Delta T \quad \cdots\cdots(2)$$

C_v = molar specific heat at constant volume
C_p = molar specific heat at constant pressure

- Q in Eqn (2) is greater than Q in Eqn (1) for a given *n* and ΔT. Why?

Ideal Monatomic Gas

- Monatomic gas: one atom per molecule.
- When energy is added to a monatomic gas in a container with a fixed volume, all of the energy goes into increasing the translational kinetic energy of the gas.
- There is no other way to store energy in such a gas.

Exercise on Molar Specific Heat

Find:

(a) C_v (molar specific heat at constant volume, State $i \to f$);

(b) C_p (molar specific heat at constant pressure, , State $i \to f'$) of an ideal monatomic gas.

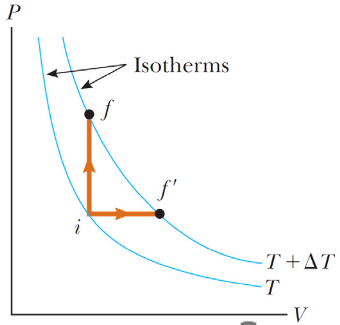
Express your answers in terms of R (Universal Gas Constant).

Answers:

$C_v = 3R/2$

$C_p = 5R/2$

Remark: $\gamma = \dfrac{C_p}{C_v} = \dfrac{5}{3}$



Molar Specific Heat of Monatomic Gases

- Constant Volume:

$$C_v = \frac{3R}{2} = 12.5\ \mathrm{J/(mol \cdot K)}$$

- Constant Pressure:

$$C_p = \frac{5R}{2} = 20.8\ \mathrm{J/(mol \cdot K)}$$

- Applicable to any ideal gas:

$$C_p - C_v = R$$

Molar Specific Heat of Various Gases

Molar Specific Heats of Various Gases

Gas	Molar Specific Heat (J/mol · K)[a] C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

[a] All values except that for water were obtained at 300 K.

Quick Quiz

1) How does the internal energy (E_{int}) of an ideal gas change as it follows path $i \to f$?
2) How does the internal energy of an ideal gas change as it follows path $f \to f'$ along the isotherm labeled T + ΔT?

(A) E_{int} increases.

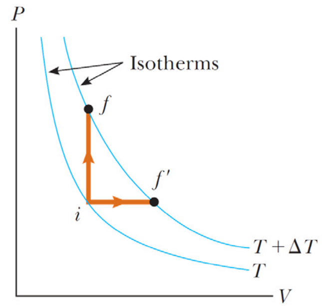
(B) E_{int} decreases.

(C) E_{int} stays the same.

Answers:

1)

2)



Exercise: Heating a cylinder of helium gas

A cylinder contains 3 moles helium gas at 300 K.

i. The gas is heated at constant volume, calculate the heat required to transfer to the gas in order to increase the temperature to 500 K.

ii. The gas is heated at constant pressure, calculate the heat required to transfer to the gas in order to increase the temperature to 500 K.

Adiabatic Processes

- Adiabatic process: No energy is transferred by heat between a system and its surroundings.
- Assume an ideal gas is in an equilibrium state and $PV = nRT$ is valid.
- The pressure and volume of an ideal gas at any time during an adiabatic process are related by PV^{γ} = constant.
- $\gamma = C_P / C_V$ is assumed to be constant during the process.
- All three variables in the ideal gas law (P, V, T) can change during an adiabatic process.

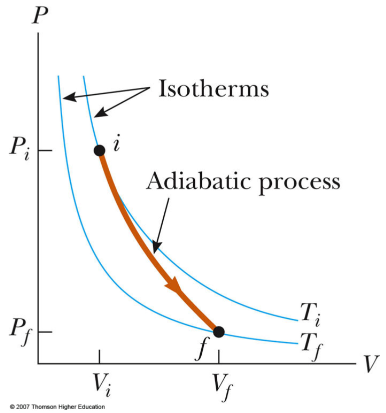
Exercise: Adiabatic Process

Considering an ideal gas undergoes an adiabatic process, prove:

i. $PV^{\gamma} = \text{constant}$

ii. $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$

where $\gamma = C_P / C_V$.

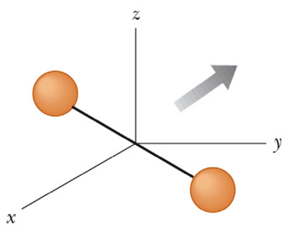


Exercise: Diesel Engine Cylinder

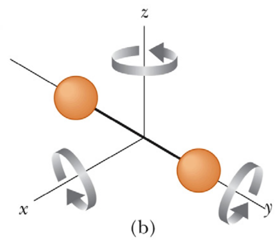
Air (20°C) in a diesel engine cylinder is compressed from an initial pressure of 1 atm and a volume of 800 cm^3 to 60 cm^3. Assume air behaves as an ideal gas with $\gamma = 1.4$ and the compression is adiabatic. Find the final pressure and temperature of the air.

Equipartition of Energy

- In addition to internal energy, one possible energy is the translational motion of the center of mass.
- Rotational motion about the various axes also contributes.
- For this molecule, we can neglect the rotation around the *y* axis since it is negligible compared to the *x* and *z* axes.



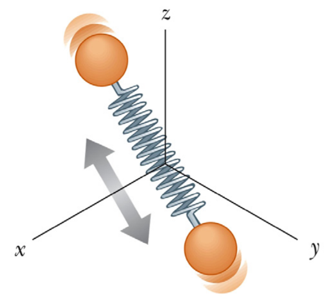
(a)



(b)

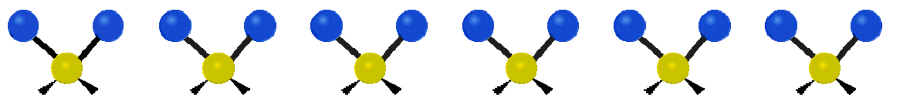
Equipartition of Energy

- The molecule can also vibrate.
- There is kinetic energy and potential energy associated with the vibrations.



(c)

Molecular Vibrations



Symmetrical Stretching	Antisymmetrical Stretching	Scissoring	Rocking	Wagging	Twisting

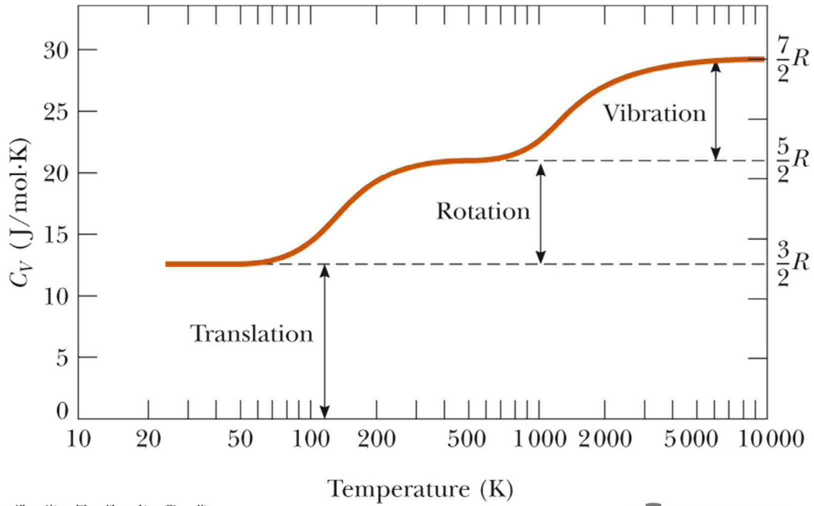
Animation Source: Wikipedia

Equipartition of Energy

- Translational motion: 3 degrees of freedom.
- Rotational motion: 2 degrees of freedom.
- Vibrational motion: 2 degrees of freedom.
- Suppose: $E_{\text{int}} = \underbrace{3N\left(\frac{1}{2}k_BT\right)}_{\text{Translational}} + \underbrace{2N\left(\frac{1}{2}k_BT\right)}_{\text{Rotational}} + \underbrace{2N\left(\frac{1}{2}k_BT\right)}_{\text{Vibrational}}$

$$C_v = \frac{1}{n}\frac{dE_{\text{int}}}{dT} = \frac{7R}{2}$$

Molar specific heat of hydrogen as a function of temperature. Hydrogen liquefies at 20 K.

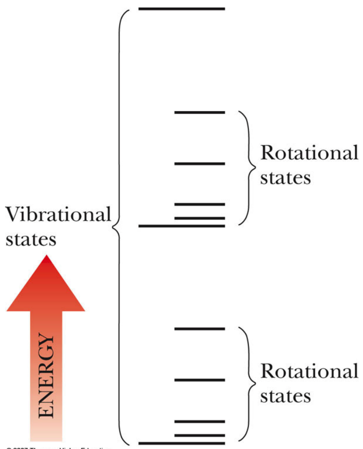


Complex Molecules

- For molecules with more than two atoms, the vibrations are more complex.
- The number of degrees of freedom is larger.
- The more degrees of freedom available to a molecule, the more vibration modes there are to store energy.
  - This results in a higher molar specific heat.

Quantization of Energy

- Vibrational states are separated by larger energy gaps than are rotational states.
- At low temperatures, the energy gained during collisions is generally not enough to raise it to the first excited state of either rotation or vibration.



Quantization of Energy

- As the temperature increases, the speed (or energy) of the molecules increases.
- In some collisions, the molecules have enough energy to excite to the first excited state.
- As the temperature continues to increase, more molecules are in excited states.

Quantization of Energy

- ~ Room temperature, rotational energy contributes fully to the internal energy.
- ~ 1000 K, vibrational energy levels are reached.
- ~10,000 K, vibration contributes fully to the internal energy.

Monatomic Gas	Diatomic Gas	
	Room Temperature	High Temperature
C_v = 3R/2 C_p = 5R/2 γ = 5/3 = 1.67	C_v = 5R/2 C_p = 7R/2 γ = 7/5 = 1.4	C_v = 7R/2
Translational only	Translational and Rotational	Translational, Rotational, and Vibrational

Quick Quiz

The molar specific heat of a diatomic gas is measured at constant volume and found to be 29.1 J/(mol·K). What are the types of energy that are contributing to the molar specific heat?

A. Translation only.
B. Translation and rotation only.
C. Translation and vibration only.
D. Translation, rotation, and vibration.

Answer:

Quick Quiz

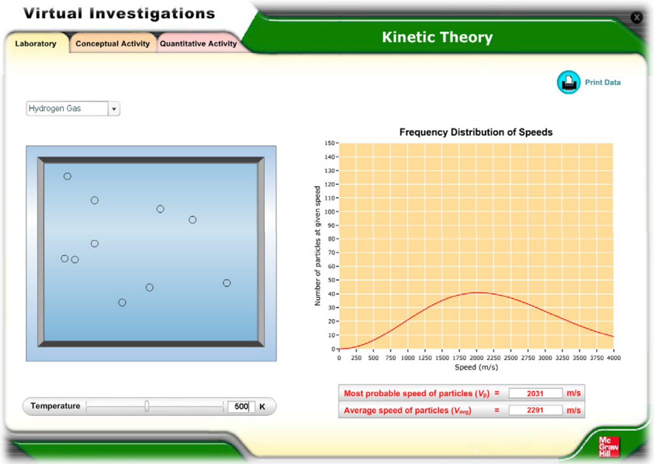
The molar specific heat of a gas is measured at constant volume and found to be 11R/2. Is the gas most likely to be

A. monatomic,
B. diatomic, or
C. polyatomic?

Answer: C [C_v = 11R/2, which is larger than the highest possible value of C_v (7R/2) for a diatomic gas]

Web Resource: Kinetic Theory

Web Resource



http://www.mhhe.com/biosci/genbio/virtual_labs/kinetic_theory_phy/main.swf

Boltzmann Distribution Law

Probability of finding a molecule in a particular energy state:

$$n_v(E) = n_o \exp\left(-\frac{E}{k_B T}\right)$$

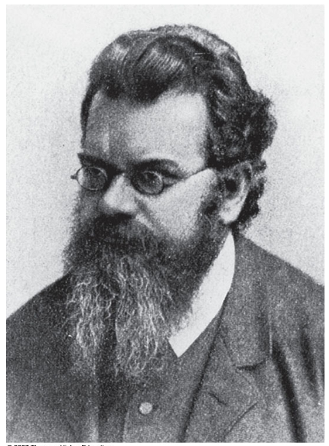
where $n_V(E)\,dE$ is the number of molecules per unit volume with energy between E and $E + dE$.

Exercise on Number Density

Consider a gas at a temperature of 2500 K whose atoms can occupy only two energy levels separated by 1.5 eV. Determine the ratio of the number of atoms in the higher energy level to the number in the lower energy level.

Ludwig Boltzmann

- 1844 – 1906
- Austrian physicist
- Contributed to:
  - Kinetic Theory of Gases.
  - Electromagnetism.
  - Thermodynamics.
- Pioneer in statistical mechanics.



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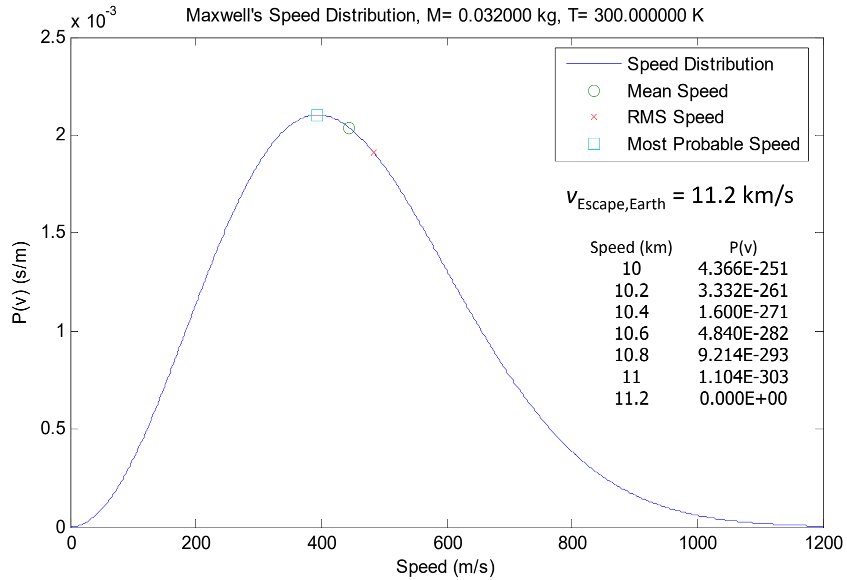
Maxwell-Boltzmann Speed Distribution

- Distribution of speeds in *N* gas molecules:

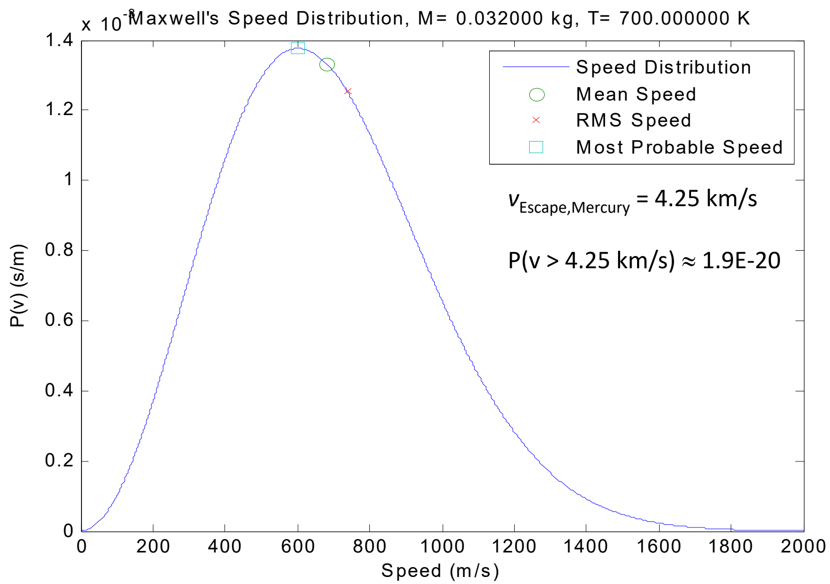
$$N_v = 4\pi N\left(\frac{m_o}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{m_o v^2}{2k_B T}\right)$$

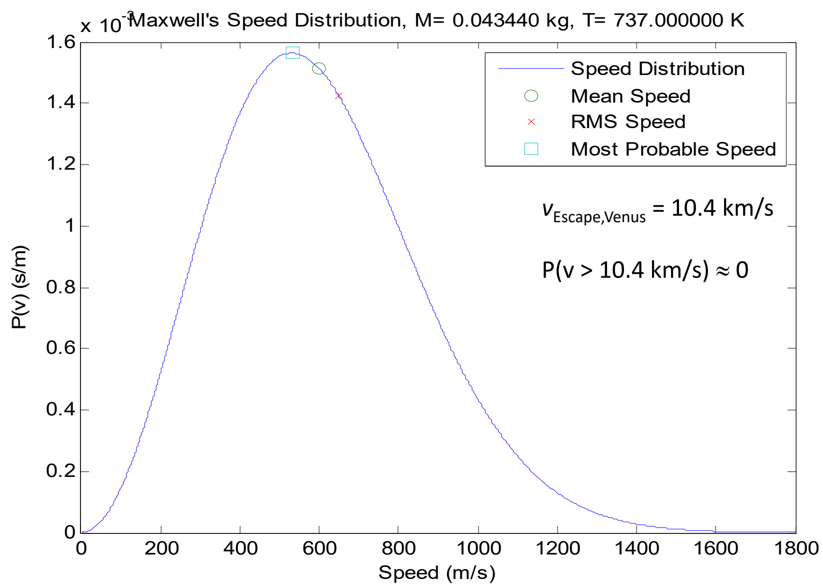
$$P(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(-\frac{Mv^2}{2RT}\right) \qquad \int_0^\infty P(v)\,dv = 1$$

M = Molar Mass of the Gas [kg],
R = Gas Constant = 8.31 J/(mol·K),
T = Temperature [K], and
v = Speed of Gas Molecules.



Speed (km)	P(v)
10	4.366E-251
10.2	3.332E-261
10.4	1.600E-271
10.6	4.840E-282
10.8	9.214E-293
11	1.104E-303
11.2	0.000E+00





Distribution of Molecular Speeds

- Fraction of molecules with speeds in an interval [v_1, v_2]:

$$\text{Fraction}[v_1, v_2] = \int_0^\infty P(v)\, dv$$

- Mean Speed:

$$\bar{v} = \int_0^\infty v \cdot P(v)\, dv = \sqrt{\frac{8RT}{\pi M}}$$

- RMS Speed:

$$\bar{v}^2 = \int_0^\infty v^2 P(v)\, dv = \frac{3RT}{M}$$

$$v_{\text{RMS}} = \sqrt{\frac{3RT}{M}}$$

Distribution of Molecular Speeds

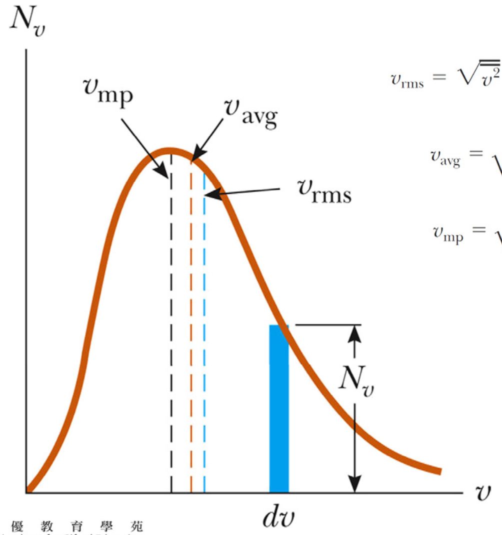
- Most Probable Speed (v_{mp}): The speed at which $P(v)$ is maximum.

$$\text{Solve } \frac{dP(v)}{dv} = 0$$

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

- Note: $v_{mp} < \bar{v} < v_{\text{RMS}}$

Maxwell-Boltzmann Speed Distribution



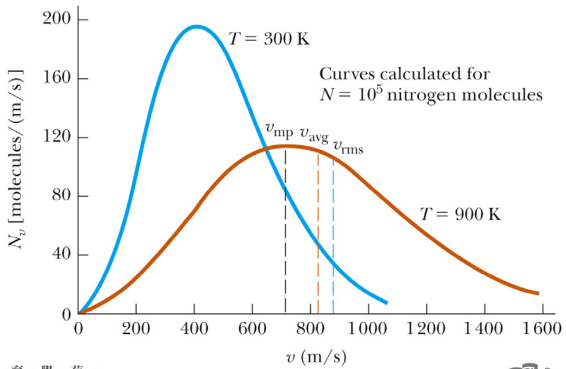
$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m_0}} = 1.73\sqrt{\frac{k_B T}{m_0}}$$

$$v_{\text{avg}} = \sqrt{\frac{8k_B T}{\pi m_0}} = 1.60\sqrt{\frac{k_B T}{m_0}}$$

$$v_{\text{mp}} = \sqrt{\frac{2k_B T}{m_0}} = 1.41\sqrt{\frac{k_B T}{m_0}}$$

Speed Distribution

- As T increases, the peak shifts to the right.
  - This shows that the average speed increases with increasing temperature.



Exercise

0.5 mole hydrogen gas at 300 K.

(a) Find the mean speed, the rms speed, and the most probable speed.

(b) Find the number of hydrogen molecules with speeds between 400 ms^{-1} and 401 ms^{-1}.

Answers:

(a) 1.78 km/s, 1.93 km/s, 1.57 km/s

(b) 2.61×10^{19} molecules.

Summary

The pressure of N molecules of an ideal gas contained in a volume V is

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m_0\overline{v^2}\right)$$

The average translational kinetic energy per molecule of a gas, $\frac{1}{2}m_0\overline{v^2}$, is related to the temperature T of the gas through the expression

$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_BT$$

where k_B is Boltzmann's constant. Each translational degree of freedom (x, y, or z) has $\frac{1}{2}k_BT$ of energy associated with it.

The internal energy of N molecules (or n mol) of an ideal monatomic gas is

$$E_{int} = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$

The change in internal energy for n mol of any ideal gas that undergoes a change in temperature ΔT is

$$\Delta E_{int} = nC_V\,\Delta T$$

where C_V is the **molar specific heat at constant volume.**

Summary

The molar specific heat of an ideal monatomic gas at constant volume is $C_V = \frac{3}{2}R$; the molar specific heat at constant pressure is $C_P = \frac{5}{2}R$. The ratio of specific heats is given by $\gamma = C_P/C_V = \frac{5}{3}$.

If an ideal gas undergoes an adiabatic expansion or compression, the first law of thermodynamics, together with the equation of state, shows that

$$PV^\gamma = \text{constant}$$

The **Boltzmann distribution law** describes the distribution of particles among available energy states. The relative number of particles having energy between E and $E + dE$ is $n_V(E)\ dE$, where

$$n_V(E) = n_0 e^{-E/k_BT}$$

The **Maxwell–Boltzmann speed distribution function** describes the distribution of speeds of molecules in a gas:

$$N_v = 4\pi N\left(\frac{m_0}{2\pi k_BT}\right)^{3/2} v^2 e^{-m_0v^2/2k_BT}$$

Equation 21.24 enables us to calculate the **root-mean-square speed**, the **average speed**, and the **most probable speed** of molecules in a gas:

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m_0}} = 1.73\sqrt{\frac{k_BT}{m_0}}$$

$$v_{avg} = \sqrt{\frac{8k_BT}{\pi m_0}} = 1.60\sqrt{\frac{k_BT}{m_0}}$$

$$v_{mp} = \sqrt{\frac{2k_BT}{m_0}} = 1.41\sqrt{\frac{k_BT}{m_0}}$$