

CHM3400 Resources

Chapter 1: Gases



Perfect Gases: Introduction

Gas: A Form of matter that fills the container it occupies.

Macroscopic Properties:

- Properties of bulk gases
- Observable: P , V , m , T

Microscopic Properties:

- Properties at the molecular level
- Not readily observable
- Mass of molecule, molecular speed, energy, collision frequency



Boyle's Law (1662)

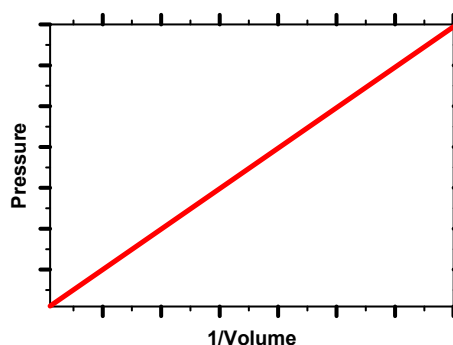
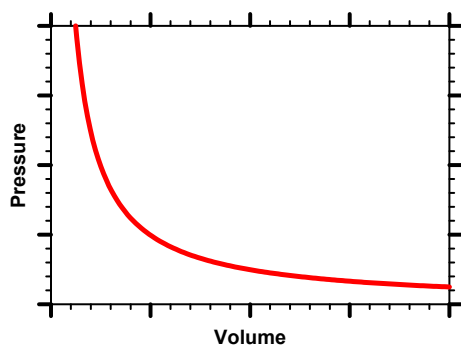
Constants: m, T

Variables: P, V

$$P_1 V_1 = P_2 V_2$$

$$PV = \text{constant}$$

$$P \propto \frac{1}{V}$$



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Charles's Law (1780)

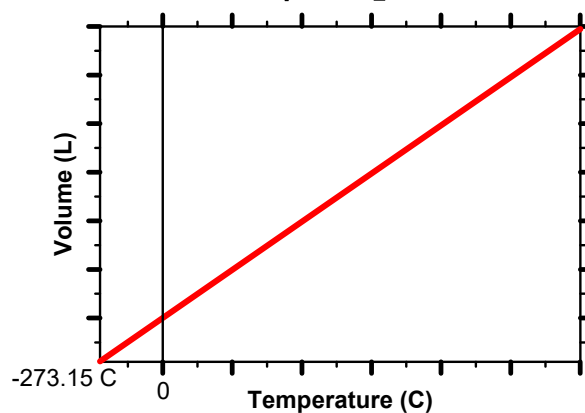
Constants: m, P

Variables: V, T

$$V_1 T_2 = V_2 T_1$$

$$V/T = \text{constant}$$

$$V \propto T$$



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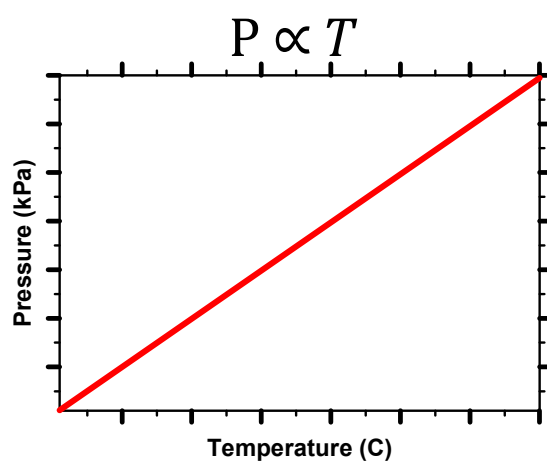
Gay-Lussac's Law (1801)

Constants: m , V

Variables: P , T

$$P_1 T_2 = P_2 T_1$$

$$P/T = \text{constant}$$



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Avogadro's Principle (1811)

Constants: P , T

Variables: n , V

If $V_1 = V_2$

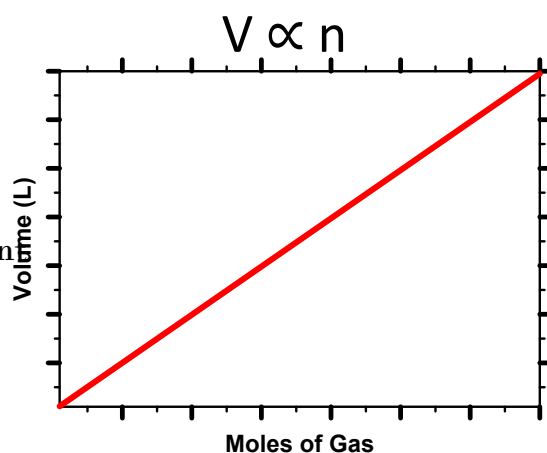
$$T_1 = T_2$$

$$P_1 = P_2$$

of molecules in
each case is constant

$$V_1 n_2 = V_2 n_1$$

$$V/n = \text{constant}$$



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Combining all Laws

$$PV = \text{Constant}$$

$$V/T = \text{Constant}$$

$$P/T = \text{Constant}$$

$$V/n = \text{Constant}$$

PV/RT = Constant ← We will define this constant as 'R' the **Gas Constant**

$$R = \frac{PV}{nT} \quad R = 8.341 \text{ kPa L mol}^{-1} \text{ K}^{-1}$$

N – number of molecules

k – Boltzmann Constant

$$k = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$$

$$k = \frac{PV}{NT}$$

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Dalton's Law: Perfect Mixtures

- In a gas mixture, each component exerts the pressure it would independent of the other gases (Each component acts as if it were alone in the container).

$$P_{\text{total}} = \Sigma P_i$$

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_n$$

$$P = nRT/V$$

$$n_{\text{total}} RT/V = n_1 RT/V + n_2 RT/V + n_3 RT/V + \dots + n_n RT/V \quad RT/V \text{ is constant}$$

$$n_{\text{total}} RT/V = (RT/V)(n_1 + n_2 + n_3 + \dots + n_n)$$

$$\chi_i = n_i/n_{\text{total}} \leftarrow \text{Mole fraction} \quad 1 = \Sigma \chi_i$$

$$P_{\text{total}} = P_{\text{total}}(\chi_1 + \chi_2 + \chi_3 + \dots + \chi_n)$$

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Gases at a Molecular Level

Kinetic Theory of Gases: Assumptions

1. A gas is made of a large number of extremely small particles which act as points (simplified model of atoms or molecules)
2. Molecules occupy little volume (most of the container is free space)
3. Molecules are in constant, random straight line motion
4. Molecules collide with one another and with the walls of the container
5. There are no forces between molecules
6. Individual molecules can gain or lose energy through collisions, but the total energy remains the same

This theory provides information on the speeds of the molecules, the frequency with which they collide, and the distribution of energy.

Seeks to explain bulk properties ($P = nRT/V$)

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Pressure of a Gas

Pressure is the manifestation of collisions with the walls of the container. Hence, if we can determine the force with which the molecules hit the wall we can determine the pressure.

N molecules of mass m , in a container of volume V , moving with a root mean speed v (though each molecule will have a different speed).

$$P = \frac{1}{3}Nm\bar{v}^2/V$$

$$PV = \frac{1}{3}Nm\bar{v}^2$$

PV is a constant at constant T . If \bar{v}^2 is constant, this is Boyle's Law

We will not prove this, but, will assume it is true, and use the PV equations from macroscopic and microscopic sections to understand the relationship between speed, temperature, energy, and collision frequency.

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Temperature, and Kinetic Energy

$$E_{\text{kin}} = \frac{1}{2}mv^2,$$

$$\text{Average } E_{\text{kin}} = \frac{1}{2}m\bar{v}^2$$

Therefore, the average E_{kin} of a molecule is:

$$E_{\text{kin}} = \frac{1}{2}N_a m\bar{v}^2; N_a - \text{Avogadro's Number}$$

$$m\bar{v}^2 = 2E_{\text{kin}}/N_a; \text{ substitute into } PV = \frac{1}{3}Nm\bar{v}^2$$

$$PV = \frac{2}{3}NE_{\text{kin}}/N_a; PV = nRT$$

$$nRT = \frac{2}{3}NE_{\text{kin}}/N_a; n = N/N_a$$

$$RT = \frac{2}{3}E_{\text{kin}}$$

or...

$$E_{\text{kin}} = \frac{3}{2}RT \leftarrow \text{Average Kinetic energy of a Particle}$$

Temperature of the gas is a measure of the kinetic energy of the molecules.

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Temperature, Speed, and Kinetic Energy

Determining the average speed of a particle

$$\text{Combine } E_{\text{kin}} = \frac{1}{2}N_a m\bar{v}^2 \text{ and } E_{\text{kin}} = \frac{3}{2}RT$$

$$\frac{1}{2}N_a m\bar{v}^2 = \frac{3}{2}RT$$

$$\bar{v}^2 = 3RT/N_a m; M = N_a m$$

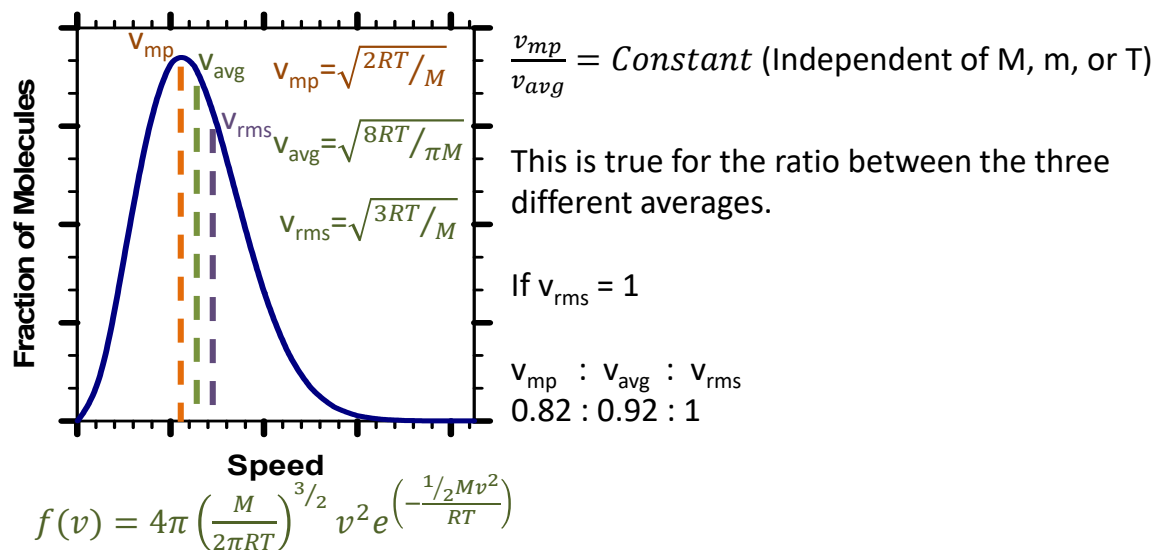
$$\bar{v}^2 = 3RT/M \leftarrow \text{Speed of an average particle}$$

$$v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{3RT/M}$$

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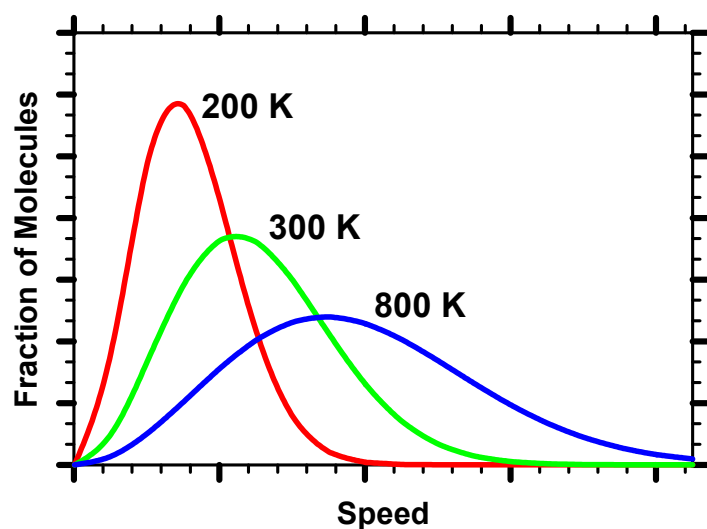
Distribution of Molecular Speeds



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Distribution of Molecular Speeds with Temperature



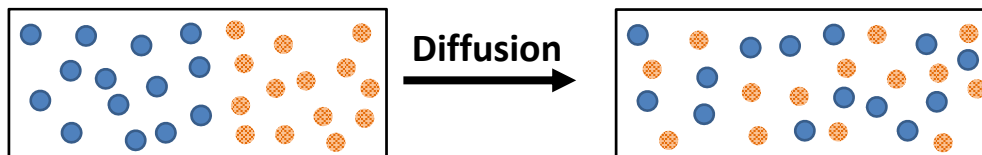
Speed	Fraction
0	1
v_{avg}	0.5
$3v_{avg}$	0.45×10^{-3}
$5v_{avg}$	40×10^{-10}
$10v_{avg}$	4×10^{-43}

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Diffusion and Effusion

Diffusion: The mixing of different molecules in the absence of any mechanical mixing.



Effusion: The 'escape' of a gas through a small hole.



$$\text{Rate of effusion} \propto 1/\sqrt{M}$$

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Molecular Collisions

- The frequency with which molecules undergo collisions (z) is dependent upon the molecular density of the gas (n - number of molecules/Volume), and, how fast they are moving (v).
- The units are therefore z in # of collisions/ $\text{m}^2 \cdot \text{s}^{-1}$

$$z \propto nv$$

- For collisions with the wall of the container:

$$z_{\text{wall}} = \frac{1}{4}nv_{\text{avg}}$$

If you have two gases A and B:

$$\frac{z_{\text{wall}}(A)}{z_{\text{wall}}(B)} = \frac{\frac{1N_A}{4V} \sqrt{\frac{8RT}{\pi M_A}}}{\frac{1N_B}{4V} \sqrt{\frac{8RT}{\pi M_B}}} \quad n = \frac{N}{V}, \text{ or } P/kT$$

$$V_{\text{avg}} = \sqrt{8RT/\pi M}$$

$$\frac{z_{\text{wall}}(A)}{z_{\text{wall}}(B)} = \frac{N_A}{N_B} \sqrt{\frac{M_B}{M_A}}$$

$$\frac{z_{\text{wall}}(A)}{z_{\text{wall}}(B)} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}}$$

Note that the ratio of the number of molecules of A and B is the ratio of the partial Pressures

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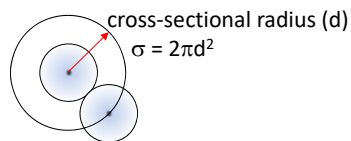


Molecular Collisions

- For collisions between similar molecules, we need to use the mean relative speed (perhaps one is heavier than the other in a mixture, resulting in it having a slower mean speed). We define this as the mean relative speed.

$$v_{rel,mean} = \sqrt{8RT/\pi\mu}, \text{ where } \mu = \frac{M_A M_B}{M_A + M_B}$$

If $M_A = M_B$, $\mu = \sqrt{2}$, and $v_{rel,mean} = \sqrt{2}v_{mean}$



Therefore, the collision frequency (Z_A) not only depends upon the relative speed, but, the size (or, cross-section) of the molecules

$$Z_A = n\sigma v_{rel,mean}$$

$$Z_A = \sqrt{2}n\sigma v_{mean} \quad Z_A = \sqrt{2}\pi d^2 \left(\frac{N}{V}\right) v_{mean}$$

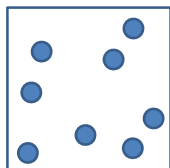
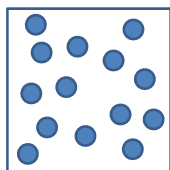
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How far does a gas molecule travel before colliding with another molecule?

Mean Free Path – Average distance a molecule travels between collisions, and is often represented as λ .

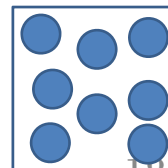
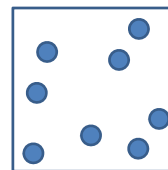
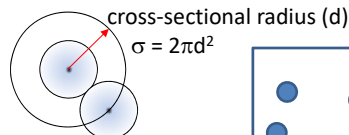
λ is inversely proportional to the molecular density (n - molecules/volume), and, the size of the molecules (σ - cross section).



$$\lambda \propto \frac{1}{n\sigma}$$

$$\lambda = \frac{1}{\sqrt{2}n\sigma}, n = \frac{N}{V}, \text{ or } P/kT$$

$$\lambda = \frac{kT}{\sqrt{2}\sigma P}$$



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Real Gases

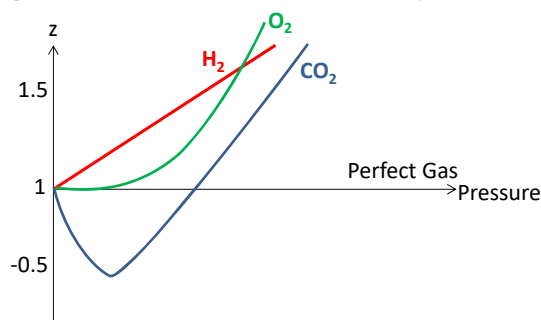
- The Gas Laws were obtained from experiments performed under ‘normal’ Temperature and Pressure conditions.
- Under extreme conditions, we observe deviations from these laws.

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Compressibility Factor

- One way to measure deviation from ideal/perfect behavior.
- Compressibility factor defined as ‘z’, where $z = PV/nRT$ ($z = 1$ for a perfect gas)
- Different gases deviate in different ways



- The compressibility factor is an empirical (experimental) prediction of real gas behavior, but, it doesn't tell us anything about WHY we see deviations

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Modifications to the Kinetic Theory of Gases

- Needs to modify the ideal gas law to account for deviations.
- Assumption of the Kinetic Theory:

Molecules occupy very little volume.

- What if we allow them to have a volume 'b' in $\text{L}\cdot\text{mol}^{-1}$
 - The molecules then have less volume in which to move so:

$$V_{\text{real}} = V_{\text{measured}} - nb$$

$PV = nRT$ becomes

$$P(V - nb) = nRT$$

$$PV = nRT + Pnb \text{ (divide by } nRT)$$

$$z = PV/nRT$$

$$Z = 1 + \frac{bP}{RT}$$

This fits real behavior where $Z > 1$ (high pressure deviations), but not all pressures...we need more!

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Modifications to the Kinetic Theory of Gases

- Assumption of the Kinetic Theory:

*There are **no forces** between molecules*

- What if we account for Van der Waal forces between molecules?

- These are attractive forces in the liquid phase.
- Can cause a gas to condense with enough pressure.
- This will cause the number of collisions with the walls to decrease, and, the force of each collision with the wall will also decrease (since the molecule feels an attraction to another molecule away from the wall)
- Thus, the observed pressure will be lower than that of a 'perfect' gas.

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Modifications to the Kinetic Theory of Gases

Including Van der Waal forces

- Decrease in observed pressure will depend upon $(n/V)^2$, one n/V for the decrease in the number of collisions, and one for the decrease in force of each collision.

$$P_{\text{ideal}} = P_{\text{real}} + a(n/V)^2$$

$$\text{Using } P(V-nb) = nRT$$

$$(P + a(n/V)^2)(V - nb) = nRT$$

$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

$$Z = \frac{PV}{nRT} = \frac{V}{V-nb} - \frac{an}{RTV}$$

The first term provides provides $Z > 1$ deviations, while the second term provides $Z < 1$ deviations.

$Z > 1$ deviations are due to molecules having finite size and is quantified by 'b'.

$Z < 1$ deviations are due to intermolecular forces that are quantified by 'a'.

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