Chapter 5

The Gas Laws

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Pressure

- **Force per unit area.**
- **Gas molecules fill container.**
- **Molecules move around and hit sides.**
- **Collisions are the force.**
- **Container has the area.**
- **Measured with a barometer.**

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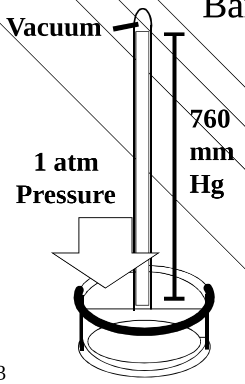
Barometer



- **The pressure of the atmosphere at sea level will hold a column of mercury 760 mm Hg.**
- **1 atm = 760 mm Hg**

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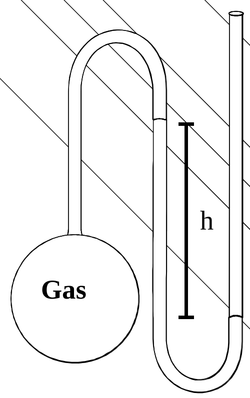
Manometer



- **Column of mercury to measure pressure.**
- **h is how much lower the pressure is than outside.**

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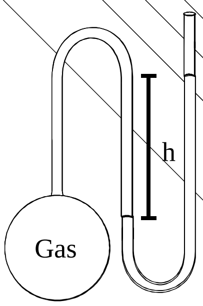
Manometer



- **h is how much higher the gas pressure is than the atmosphere.**

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Units of pressure

- **1 atmosphere = 760 mm Hg**
- **1 mm Hg = 1 torr**
- **1 atm = 101,325 Pascals = 101.325 kPa**
- **Can make conversion factors from these.**
- **What is 724 mm Hg in kPa?**
- **in torr?**
- **in atm?**

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The Gas Laws

- **Boyle's Law**
- **Pressure and volume are inversely related at constant temperature.**
- **PV= k**
- **As one goes up, the other goes down.**
- **$P_1V_1 = P_2 V_2$**
- **Graphically**

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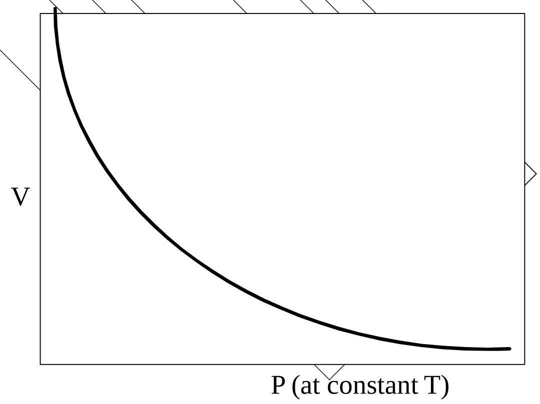

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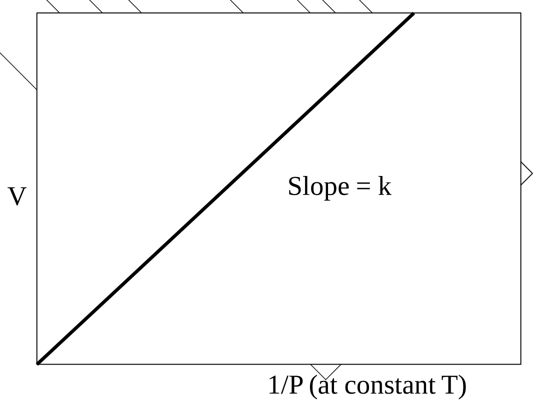

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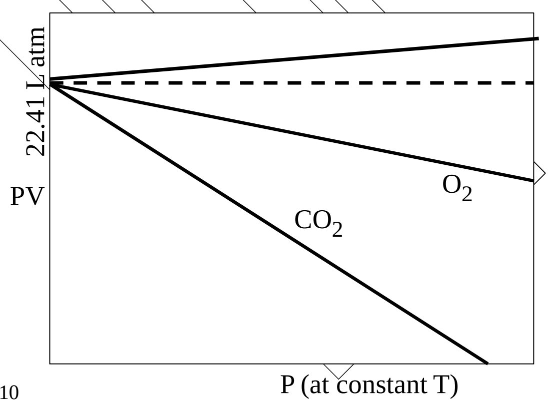

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Examples

- **20.5 L of nitrogen at 25ºC and 742 torr are compressed to 9.8 atm at constant T. What is the new volume?**
- **30.6 mL of carbon dioxide at 740 torr is expanded at constant temperature to 750 mL. What is the final pressure in kPa?**

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Charles' Law

- **Volume of a gas varies directly with the absolute temperature at constant pressure.**
- **V = kT (if T is in Kelvin)**
- **$\frac{V_1}{T_1} = \frac{V_2}{T_2}$**
- **Graphically**

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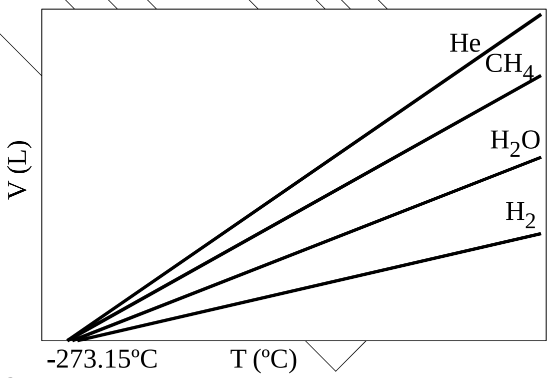

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Examples

- **What would the final volume be if 247 mL of gas at 22ºC is heated to 98ºC , if the pressure is held constant?**

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Examples

- **At what temperature would 40.5 L of gas at 23.4ºC have a volume of 81.0 L at constant pressure?**

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Avogadro's Law

- **Avagadro's**
- **At constant temperature and pressure, the volume of gas is directly related to the number of moles.**
- **V = k n (n is the number of moles)**
- $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

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Gay- Lussac Law

- **At constant volume, pressure and absolute temperature are directly related.**
- **P = k T**
- $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

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Combined Gas Law

- **If the moles of gas remains constant, use this formula and cancel out the other things that don't change.**
- $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

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Examples

- A deodorant can has a volume of 175 mL and a pressure of 3.8 atm at 22ºC. What would the pressure be if the can was heated to 100.ºC?
- What volume of gas could the can release at 22ºC and 743 torr?

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Ideal Gas Law

- PV = nRT
- V = 22.42 L at 1 atm, 0ºC, n = 1 mole, what is R?
- R is the ideal gas constant.
- R = 0.08206 L atm/ mol K
- Tells you about a gas is NOW.
- The other laws tell you about a gas when it changes.

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Ideal Gas Law

- An *equation of state.*
- Independent of how you end up where you are at.
- Does not depend on the path.
- Given 3 you can determine the fourth.
- An Empirical Equation - based on experimental evidence.

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Ideal Gas Law

- A hypothetical substance - the ideal gas
- Think of it as a limit.
- Gases only approach ideal behavior at low pressure (< 1 atm) and high temperature.
- Use the laws anyway, unless told to do otherwise.
- They give good estimates.

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Examples

- A 47.3 L container containing 1.62 mol of He is heated until the pressure reaches 1.85 atm. What is the temperature?
- Kr gas in a 18.5 L cylinder exerts a pressure of 8.61 atm at 24.8ºC What is the mass of Kr?
- A sample of gas has a volume of 4.18 L at 29ºC and 732 torr. What would its volume be at 24.8ºC and 756 torr?

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Gas Density and Molar Mass

- D = m/V
- Let M stand for molar mass
- M = m/n
- n= PV/RT
- $M = \dfrac{m}{PV/RT}$
- $M = \dfrac{mRT}{PV} = \dfrac{m}{V}\dfrac{RT}{P} = \dfrac{DRT}{P}$

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Examples

- What is the density of ammonia at 23ºC and 735 torr?
- A compound has the empirical formula CHCl. A 256 mL flask at 100.ºC and 750 torr contains .80 g of the gaseous compound. What is the molecular formula?

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Gases and Stoichiometry

- Reactions happen in moles
- At Standard Temperature and Pressure (STP, 0ºC and 1 atm) 1 mole of gas occupies 22.42 L.
- If not at STP, use the ideal gas law to calculate moles of reactant or volume of product.

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Examples

- Mercury can be achieved by the following reaction

  What volume of oxygen gas can be produced from 4.10 g of mercury (II) oxide at STP?
- At 400.ºC and 740 torr?

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Examples

- Using the following reaction

  calculate the mass of sodium hydrogen carbonate necessary to produce 2.87 L of carbon dioxide at 25ºC and 2.00 atm.
- If 27 L of gas are produced at 26ºC and 745 torr when 2.6 L of HCl are added what is the concentration of HCl?

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Examples

- Consider the following reaction

  What volume of NO at 1.0 atm and 1000ºC can be produced from 10.0 L of NH_3 and excess O_2 at the same temperature and pressure?
- What volume of O_2 measured at STP will be consumed when 10.0 kg NH_3 is reacted?

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Examples

- What mass of H_2O will be produced from 65.0 L of O_2 and 75.0 L of NH_3 both measured at STP?
- What volume Of NO would be produced?
- What mass of NO is produced from 500. L of NH_3 at 250.0ºC and 3.00 atm?

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Dalton's Law

- The total pressure in a container is the sum of the pressure each gas would exert if it were alone in the container.
- The total pressure is the sum of the partial pressures.
- $P_{Total} = P_1 + P_2 + P_3 + P_4 + P_5 ...$
- For each P = nRT/V

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Dalton's Law

- $P_{Total} = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + ...$
- In the same container R, T and V are the same.
- $P_{Total} = (n_1 + n_2 + n_3 + ...)\frac{RT}{V}$
- $P_{Total} = (n_{Total})\frac{RT}{V}$

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The mole fraction

- Ratio of moles of the substance to the total moles.
- symbol is Greek letter chi χ
- $\chi_1 = \frac{n_1}{n_{Total}} = \frac{P_1}{P_{Total}}$

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Examples

- The partial pressure of nitrogen in air is 592 torr. Air pressure is 752 torr, what is the mole fraction of nitrogen?
- What is the partial pressure of nitrogen if the container holding the air is compressed to 5.25 atm?

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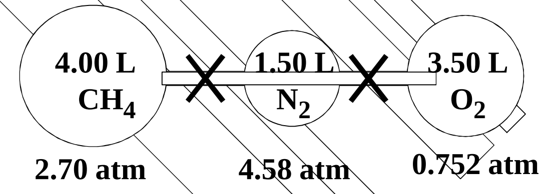
Examples



- When these valves are opened, what is each partial pressure and the total pressure?

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Vapor Pressure

- Water evaporates!
- When that water evaporates, the vapor has a pressure.
- Gases are often collected over water so the vapor pressure of water must be subtracted from the total pressure to find the pressure of the gas.
- It must be given.

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Example

- N_2O can be produced by the following reaction

  what volume of N_2O collected over water at a total pressure of 94 kPa and 22ºC can be produced from 2.6 g of NH_4NO_3? (the vapor pressure of water at 22ºC is 21 torr)

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Kinetic Molecular Theory

- Theory tells why the things happen.
- explains why ideal gases behave the way they do.
- Assumptions that simplify the theory, but don't work in real gases.

1 The particles are so small we can ignore their volume.

2 The particles are in constant motion and their collisions cause pressure.

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Kinetic Molecular Theory

3 The particles do not affect each other, neither attracting or repelling.

4 The average kinetic energy is proportional to the Kelvin temperature.

- Appendix 2 shows the derivation of the ideal gas law and the definition of temperature.
- We need the formula KE = 1/2 mv^2

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What it tells us

- $(KE)_{avg}$ = 3/2 RT
- This the meaning of temperature.
- u is the particle velocity.
- $\overline{u}$ is the average particle velocity.
- $\overline{u^2}$ is the average of the squared particle velocity.
- the root mean square velocity is

$$\sqrt{\overline{u^2}} = u_{rms}$$

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Combine these two equations

- For a mole of gas $(KE)_{avg} = N_A(\frac{1}{2}\,m\overline{u^2})$
- N_A is Avogadro's number
- $(KE)_{avg} = \frac{3}{2}\,RT$
- $N_A(\frac{1}{2}\,m\overline{u^2}) = \frac{3}{2}\,RT$

$$\overline{u^2} = \frac{3RT}{N_A m}$$

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Combine these two equations

- $\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{N_A m}} = u_{rms}$
- m is kg for one particle, so N_am is kg for a mole of particles. We will call it *M*

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

- Where *M* is the molar mass in kg/mole, and R has the units 8.3145 J/Kmol.
- The velocity will be in m/s

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Example

- Calculate the root mean square velocity of carbon dioxide at 25ºC.
- Calculate the root mean square velocity of hydrogen at 25ºC.
- Calculate the root mean square velocity of chlorine at 250ºC.

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Range of velocities

- The average distance a molecule travels before colliding with another is called the mean free path and is small (near 10^{-7})
- Temperature is an average. There are molecules of many speeds in the average.
- Shown on a graph called a velocity distribution

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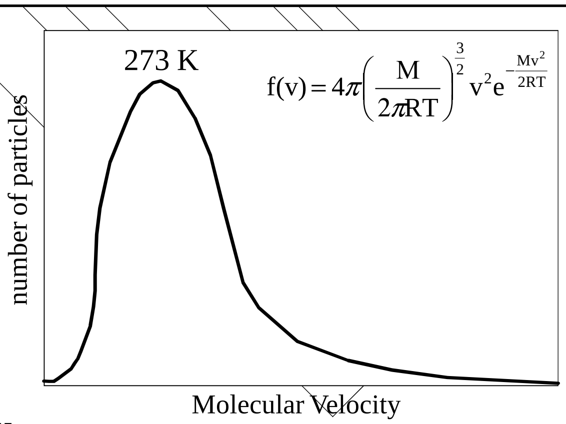

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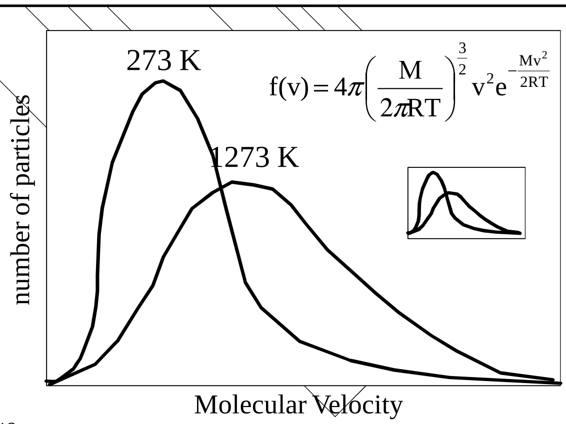

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Velocity

- Average increases as temperature increases.
- Spread increases as temperature increases.

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}}$$

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Effusion

- Passage of gas through a small hole, into a vacuum.
- The effusion rate measures how fast this happens.
- Graham's Law the rate of effusion is inversely proportional to the square root of the mass of its particles.

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Effusion

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- The effusion rate measures how fast this happens.
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$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

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Deriving

- The rate of effusion should be proportional to u_{rms}
- $\frac{\text{Effusion Rate 1}}{\text{Effusion Rate 2}} = \frac{u_{rms}\ 1}{u_{rms}\ 2}$

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Deriving

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- $\frac{\text{Effusion Rate 1}}{\text{Effusion Rate 2}} = \frac{u_{rms}\ 1}{u_{rms}\ 2}$

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Diffusion

- The spreading of a gas through a room.
- Slow considering molecules move at 100's of meters per second.
- Collisions with other molecules slow down diffusions.
- Best estimate is Graham's Law.

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Examples

- Helium effuses through a porous cylinder 3.20 time faster than a compound. What is it's molar mass?
- If 0.00251 mol of NH_3 effuse through a hole in 2.47 min, how much HCl would effuse in the same time?
- A sample of N_2 effuses through a hole in 38 seconds. what must be the molecular weight of gas that effuses in 55 seconds under identical conditions?

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Diffusion

- The spreading of a gas through a room.
- Slow considering molecules move at 100's of meters per second.
- Collisions with other molecules slow down diffusions.
- Best estimate is Graham's Law.

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Real Gases

- Real molecules do take up space and they do interact with each other (especially polar molecules).
- Need to add correction factors to the ideal gas law to account for these.

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Volume Correction

- The actual volume free to move in is less because of particle size.
- More molecules will have more effect.
- Bigger molecules have more effect
- Corrected volume $V' = V - nb$
- b is a constant that differs for each gas.
- $P' = \dfrac{nRT}{(V-nb)}$

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Pressure correction

- Because the molecules are attracted to each other, the pressure on the container will be less than ideal gas
- Depends on the type of molecule
- depends on the number of molecules per liter.
- since two molecules interact, the effect must be squared.

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Pressure correction

- Because the molecules are attracted to each other, the pressure on the container will be less than ideal
- depends on the number of molecules per liter.
- since two molecules interact, the effect must be squared.

$$P_{observed} = P' - a\left(\frac{n}{V}\right)^2$$

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Altogether

- $$P_{observed} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$
- Called the Van der Waal's equation if rearranged
- Corrected Pressure — Corrected Volume

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Where does it come from

- a and b are determined by experiment.
- Different for each gas.
- Look them up
- Bigger molecules have larger b.
- a depends on both size and polarity.
- once given, plug and chug.

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Example

- Calculate the pressure exerted by 0.5000 mol Cl_2 in a 1.000 L container at 25.0ºC
- Using the ideal gas law.
- Van der Waal's equation
  - a = 6.49 atm L^2 /mol^2
  - b = 0.0562 L/mol

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