Lecture 2

Ideal and Real Gases

Chapter 2: Properties of Gases

2.1 States of Matter

- *Characteristics of Matter.*

2.2 Gas Laws and Ideal Gas Equation

- *Boyle's Law.*
- *Charle's Law.*
- *Avogadro's Principle.*

2.3 The combined gas law

- *Values of R*
- *Gas Stoichiometry*
- *Molar Mass of a Gas*

2.4 Dalton's Law of Partial Pressure

- *Mole fractions and partial pressures*

Chapter 2: Properties of Gases

2.5 The Kinetic Molecular Theory of Gases
- *The Meaning of Temperature*

2.6 Diffusion and Effusion
- *Graham's law of Diffusion*

2.7 Real Gases and Van der Waals equation

Pressure

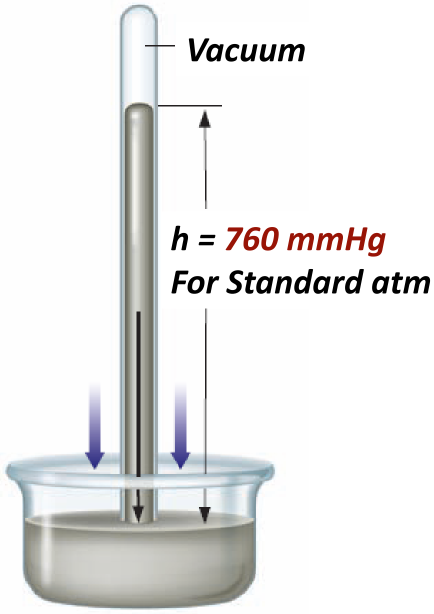
- *is the normal force exerted by a fluid (gas or liquid) per unit area.*
- *It has the unit (N/m^2), which is called a pascal (Pa).*
- *Pressure is also used on solid surfaces as synonymous to normal stress.*

  - *1 bar = 10^5 Pa = 0.1 MPa = 100 kPa*

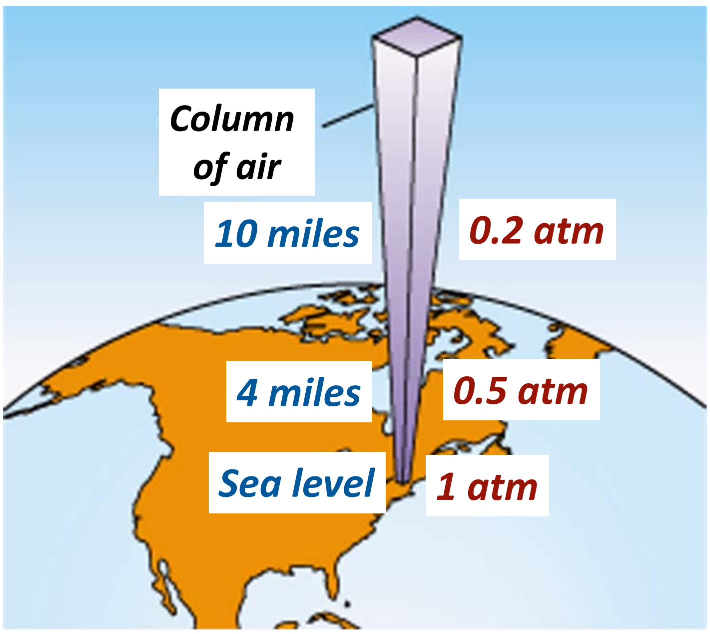
- *1 atm = 101,325 Pa = 101.325 kPa = 1.01325 bars = 760 mm Hg = 760 torr*

Measuring P: Torricelli's barometer 1643

- Gases mix completely and exert pressure on surroundings.
- Torricelli's barometer is constructed by filling a glass tube with liquid mercury and inverting it in a dish of mercury.
- At sea level the height of this column of mercury averages 760 mm.



- Pressure decreases at higher altitudes

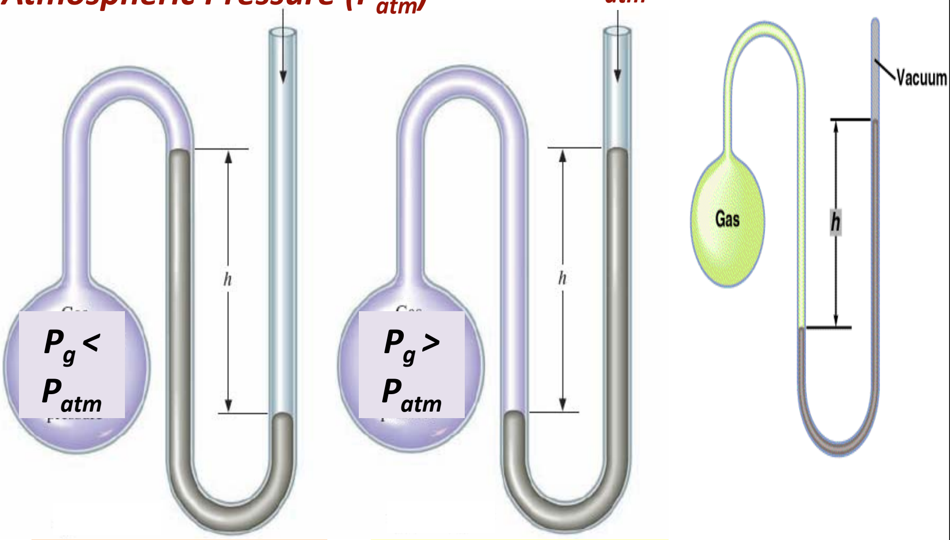


Manometers

$P_h = \rho g h$

Atmospheric Pressure (P_{atm})

P_{atm}



$P_{gas} = P_{atm} - P_h$ $\quad$ $P_{gas} = P_{atm} + P_h$ $\quad$ $P_{gas} = P_h$

- In CGS system, P is measured in dyne cm^{-2}
- The standard atmosphere is the pressure exerted by a 76 cm high column of mercury of density 13.6 g cm^{-3} in a place where the acceleration due to gravity is 980 cm s^{-2}).

$$\text{Pressure (1 atm)} = \frac{Force}{Area} = \frac{Mass \times Acceleration}{Area} = \frac{Volume \times density \times Acceleration}{Area} = Length \times density \times Acceleration =$$

$$76\ cm \times 13.6\ g\ cm^{-3} \times 980\ cm\ s^{-2}$$

$$1.01325 \times 10^6\ g\ cm^{-1} s^{-2}\ (dyne\ cm^{-2})$$

Pressure

- *In SI system, P is measured in N m⁻² (Pa: Pascal)*

$$Pressure\,(1\,atm) = \frac{Force}{Area} =$$
$$Length \times density \times Acceleration =$$
$$0.76\,m \times 1.36 \times 10^{4}\,kg\,m^{-3} \times 9.8\,m\,s^{-2}$$
$$1.01325 \times 10^{5}\,kg\,m^{-1} s^{-2}\,(N\,m^{-2})(Pa)$$

1 atm = 1.0325 bar = 760 mmHg = 760 torr = 101,325 N/m² = 101,325 Pa

Exercise (Pressure conversion)

- *The pressure of a gas is measured as 49 torr. Represent this pressure in both atmospheres and pascals?*

==

$$49\,torr \times \frac{1\,atm}{760\,torr} = 6.4 \times 10^{-2}\,atm$$

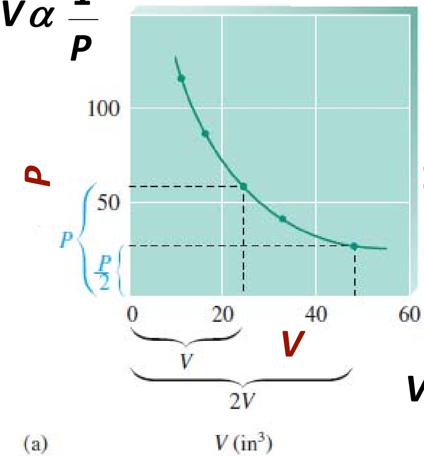
$$6.4 \times 10^{-2}\,atm \times \frac{101{,}325\,Pa}{1\,atm} = 6.5 \times 10^{3}\,Pa$$

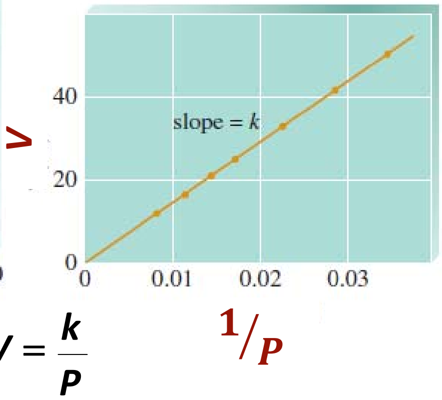
The state of a gas can be fully described in terms of 4 variables (Mass, Volume, Pressure, Temperature). By knowing 3 of them, the fourth can be calculated

Boyle's Law

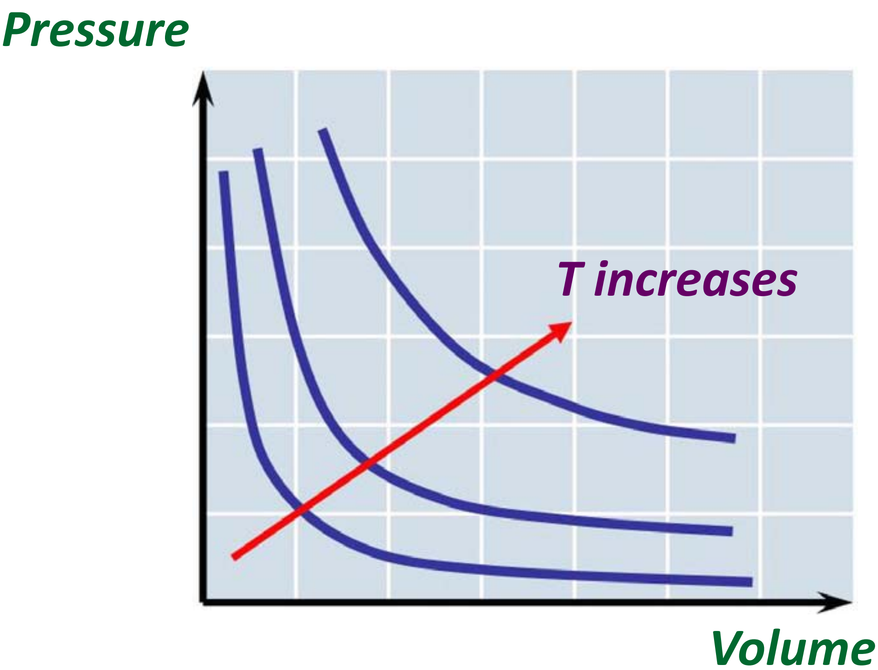
At a constant temperature, the volume of a fixed amount of gas is inversely proportional to its pressure.

$$V \alpha \frac{1}{P} \qquad PV = \text{constant} \qquad P_1V_1 = P_2V_2$$

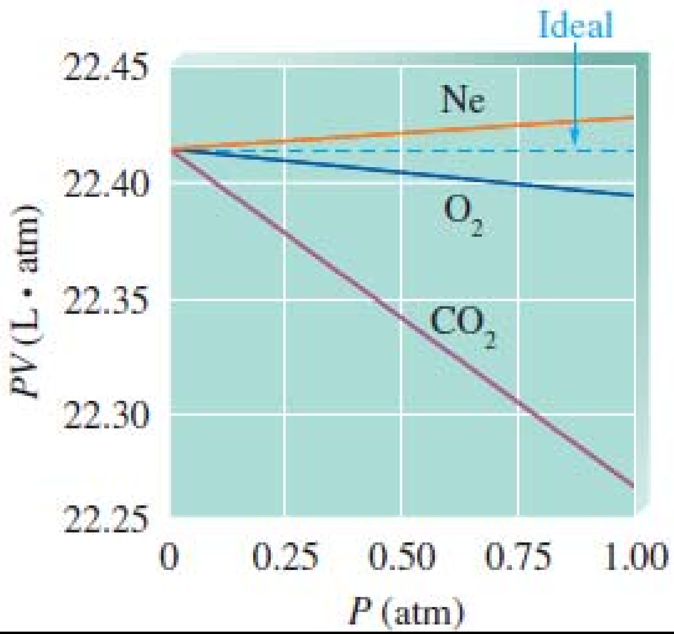




$$V = \frac{k}{P}$$



Boyle's Law holds precisely only at very low pressures



Exercise: ***Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53 L sample of gaseous SO_2 at a pressure of 5.6×10^3 Pa. If the pressure is changed to 1.5×10^4 Pa at a constant temperature, what will be the new volume of the gas?***

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Solution

$P_1 = 5.6\times10^3 Pa$ → $V_1 = 1.53L$

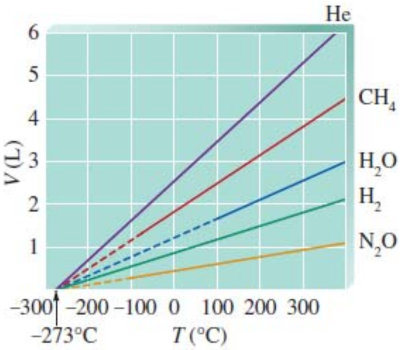
$P_2 = 1.5\times10^4 Pa$ → $V_2 = ?L$

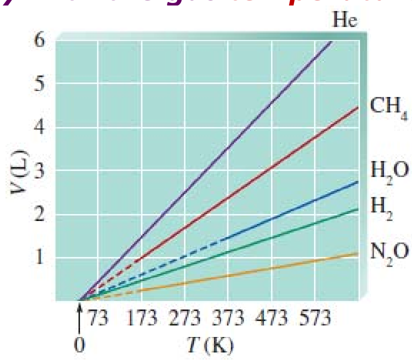
$$P_1V_1 = P_2V_2 \quad V_2 = \frac{P_1V_1}{P_2} = \frac{5.6\times10^3 \cancel{Pa}\times1.53L}{1.5\times10^4 \cancel{Pa}} = 0.57L$$

V decreases √

Charles's Law

The volume of a fixed amount of a gas at a constant pressure increases linearly with the gas temperature





✓ *Different Slopes: because of different numbers of moles of gas.*

✓ *Volumes of gases extrapolate to zero at the same temperature, –273°C = 0 K (absolute Zero)*, K = °C + 273

$V \alpha T$

$\frac{V}{T} = k$

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Exercise

A sample of gas at 15°C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38°C and 1 atm?

==

Solution

P and n = constant

$V_1 = 2.58L$ → $T_1 = 15^oC + 273 = 288K$

$V_2 = ?L$ → $T_2 = 38^oC + 273 = 311K$

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{2.58L \times 311K}{288K} = 2.79L$$

V increases √

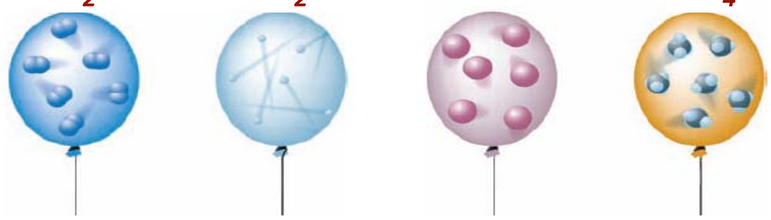
Avogadro's Law

Equal volumes of gases at the same temperature and pressure contain the same number of "particles".

OR

$V \alpha n$ $\frac{V}{n} = k$ $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

For a gas at constant T and P, the volume is directly proportional to its number of moles.



Exercise: Suppose we have a 12.2 L sample containing 0.50 mole of oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25°C. If all this O_2 were converted to 0.33 mole of ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone?

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

Solution

$V_1 = 12.2L$ → $n_1 = 0.5 \text{ mol } O_2$

$V_2 = ?L$ → $n_2 = 0.33 \text{ mol } O_3$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \qquad V_2 = \frac{V_1 n_2}{n_1} = \frac{12.2L \times 0.33 \text{ mol}}{0.5 \text{ mol}} = 8.1L$$

V decreases √

Exercise

Exercise: *Ammonia burns in oxygen to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?* $P \text{ and } T = \text{constant}$

==

Solution

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$$1 \text{ mole } NH_3 \longrightarrow 1 \text{ mole } NO$$

At constant T and P

$$1 \text{ volume } NH_3 \longrightarrow 1 \text{ volume } NO$$

The Ideal Gas Law

$$\text{Boyle's law:} \quad V = \frac{k}{P} \quad (\text{constant } T, n)$$

$$\text{Charles's law:} \quad V = bT \quad (\text{constant } P, n)$$

$$\text{Avogadro's law:} \quad V = an \quad (\text{constant } T, P)$$

$$V = R\left(\frac{Tn}{P}\right)$$

$$PV = nRT$$

Equation of state for gases

R : Universal gas constant

$$R = \frac{0.08206 \text{ L atm}}{\text{K mol}}$$

This equation is mostly obeyed at low pressures and high temperatures

Universal Gas Constant / R

$$R = \frac{PV}{nT} = \frac{1\ atm \times 22.414\ L}{1\ mol \times 273.15\ K} =$$

$$0.082057\ L\,atm\,K^{-1}\,mol^{-1}$$

$$= 82\ mL\,atm\,K^{-1}\,mol^{-1}$$

$$= 8.314\ J\,K^{-1}\,mol^{-1}$$

$$= 2.0\ cal\,K^{-1}\,mol^{-1}$$

Dalton's Law of Partial Pressures

"For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone"

Assuming ideal behavior

$$P_{Total} = P_1 + P_2 + P_3 + ...$$

$$= \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + ...$$

$$= \left(n_1 + n_2 + n_3 + ...\right)\frac{RT}{V} = \frac{n_{Total} RT}{V}$$

Dalton's Law

- *The pressure exerted by an ideal gas is not affected by the identity (composition) of the gas particles. This reveals:*
  - *The volume of the individual gas particle is not important*
  - *The forces among the particles must not be important.*

Exercise: *Mixtures of helium and oxygen can be used in scuba diving tanks to help prevent "the bends." For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O_2 at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.*

Solution

$$n_{He} = \frac{(1.0\ atm)(46\ L)}{(0.08206\ L.atm/K.mol)(298\ K)} = 1.9\ mol$$

$$n_{O_2} = \frac{(1.0\ atm)(12\ L)}{(0.08206\ L.atm/K.mol)(298\ K)} = 0.49\ mol$$

Calculate the partial pressure for each gas in the tank

$$P_{He} = \frac{(1.9\ mol)(0.08206\ L.atm/K.mol)(298\ K)}{(5\ L)} = 9.3\ atm$$

$$P_{O_2} = \frac{(0.49\ mol)(0.08206\ L.atm/K.mol)(298\ K)}{(5\ L)} = 2.4\ atm$$

$$P_T = P_{He} + P_{O_2} = 9.3 + 2.4 = 11.7\ atm$$

Mole fraction, χ

The ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

$$\chi_1 = \frac{n_1}{n_T} = \frac{n_1}{n_1 + n_2 + n_3 + ...}$$

$$= \frac{\left(V/RT\right)P_1}{\left(V/RT\right)\left(P_1 + P_2 + P_3 + ...\right)}$$

Mole fraction, χ

$$\chi_1 = \frac{P_1}{(P_1 + P_2 + P_3 + \ldots..)} = \frac{P_1}{P_T}$$

- The mole fraction of each component in a mixture of ideal gases is directly related to its partial pressure

$$\chi_2 = \frac{n_2}{n_T} = \frac{P_2}{P_T}$$

$$\sum_i \chi_i = 1$$

Example

- The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present at 25°C?

Answer

$$\chi_{O_2} = \frac{P_{O_2}}{P_T} = \frac{156\ \text{torr}}{743\ \text{torr}} = 0.210$$

Homework

A rigid 9.50 L flask contained a mixture of 3.00 moles of hydrogen (H_2) gas, 1.00 moles of oxygen (O_2) gas, and enough neon (Ne) gas so that the partial pressure of neon in the flask was 3.00 atm. The temperature was 27°C.

1) Calculate the total pressure in the flask.
2) Calculate the mole fraction of oxygen in the flask.
3) Calculate the density in (g mL^{-1}) of the mixture in the flask
4) The gas mixture is ignited by a spark and the reaction below occurs until one of the reactants is totally consumed.

$$O_2(g) + 2H_2(g) \rightarrow 2H_2O(g)$$

Give the mole fraction of all species present in the flask at the end of the reaction.

Kinetic Molecular Theory (KMT) of Gases

Postulates

1) A gas is composed of a large number of small (relative to distance between them) particles that behave like hard (point masses), spherical objects—have negligible volume
2) The particles are in constant random (straight-line) motion involving frequent elastic "particle's kinetic energy is not lost" collisions with each other and with the walls of the container (origin of pressure)
3) Attractive and repulsive forces between molecules are negligible.
4) The average kinetic energy of gas particles is directly proportional only to the absolute "Kelvin" temperature of the gas.

KMT and ideal gas laws are compatible

Boyle's Law

A decrease in volume means that the gas particles will hit the wall more often, thus increasing pressure

$$P = nRT\left(\frac{1}{V}\right)$$

Pressure and Temperature

When a gas temperature increases, the speeds of its particles increase; the particles hit the wall with greater force and greater frequency. Since the volume remains the same, this would result in increased gas pressure

$$P = \left(\frac{nR}{V}\right)T$$

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Charles's Law

If the gas Temp. increases, the particles' speed increases; thus they hit the walls more often and with more force. The only way to keep the pressure constant in this situation is to increase the volume of the container.

$$V = \left(\frac{nR}{P}\right)T$$

Avogadro's Law

The increase in the number of gas particles at the same temperature would cause the pressure to increase if the volume was constant. The only way to return the pressure to its original value is to increase the volume.

$$V = \left(\frac{RT}{P}\right)n$$

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Dalton's Law

KMT assumes that all gas particles are independent of each other and that the volumes of the individual particles are unimportant. Thus the identities of the gas particles do not matter.

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Root Mean Square Velocity

- *If $\overline{u^2}$ is the average of the square of the velocities of the particles, The quantity $\frac{1}{2}m\overline{u^2}$ will represent the average kinetic energy of a gas particle.*

- *The average kinetic energy for a mole of gas particles*

$$(KE)_{avg} = N_A\left(\frac{1}{2}m\overline{u^2}\right)$$

$$N_A m = M$$

Mass of a mole of the gas (kg)

N_A: Avogadro's number, m: mass (kg) of each particle

Root Mean Square Velocity

- $\sqrt{\overline{u^2}}$ is also called "root mean square velocity" u_{rms}:

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

$$(KE)_{avg} = {}^{3}\!/_{2}RT = N_A\left({}^{1}\!/_{2}m\overline{u^2}\right)$$

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

1 J = 1 kg m²/s²

R= 8.3145 J/K.mol

The Kinetic Molecular Theory (KMT) of Gases

- *For a large number of molecules moving in random directions:*

$$PV = \frac{1}{3}nN_A m\overline{u^2}$$

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

$$PV = \frac{1}{3}nN_A m\overline{u^2} = \frac{2}{3}nN_A\left(\frac{1}{2}m\overline{u^2}\right) = \frac{2}{3}nN_A KE = \frac{2}{3}n(KE)_{avg}$$

$$\frac{PV}{n} = \frac{2}{3}(KE)_{avg}$$

$$\frac{PV}{n}\ \alpha\ T \rightarrow \frac{PV}{n} = RT$$

$$\frac{PV}{n} = \frac{2}{3}(KE)_{avg} \qquad (KE)_{avg} = \frac{3}{2}RT \qquad \frac{PV}{n} = RT$$

Meaning of Temp.: *The Kelvin temperature is an index of the random motions of the particles of the gas.*

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

$$\sqrt{\overline{u^2}} = u_{rms} = \sqrt{\frac{3RT}{N_A m}} = \sqrt{\frac{3RT}{M}}$$

Exercise

Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C.

Solution *What is the mass of a mole of He in kilograms?*

$$M = 4.0\frac{g}{mol} \times \frac{1\,kg}{1000\,g} = 4.0 \times 10^{-3}\frac{kg}{mol}$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\left(\frac{8.314\ J}{K\ mol}\right)(298K)}{\left(4.0\times10^{-3}\frac{kg}{mol}\right)}} = \sqrt{1.86\times10^{6}\frac{J}{kg}}$$

$$= \sqrt{1.86\times10^{6}\frac{kg\ m^2}{kg\ s^2}} = \frac{1.36\times10^{3}m}{s}$$

Exercise At the same temperature, compare $U_{rms}\,H_2$ with $U_{rms}\,O_2$

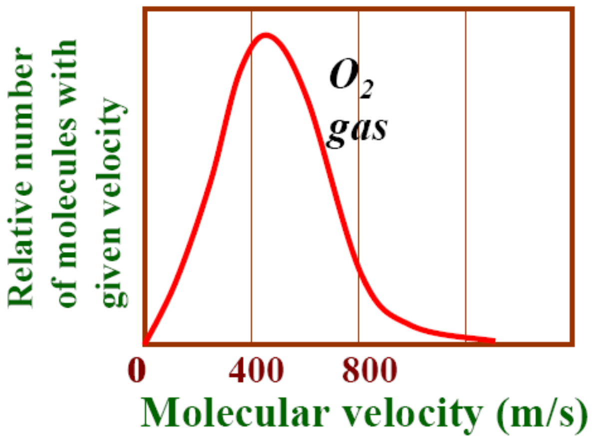
Solution

$$\frac{u_{rms}(H_2)}{u_{rms}(O_2)}=\frac{\sqrt{\dfrac{3RT}{M_{H_2}}}}{\sqrt{\dfrac{3RT}{M_{O_2}}}}=\sqrt{\frac{M_{O_2}}{M_{H_2}}}=\sqrt{\frac{32}{2}}=4$$

Hydrogen moves 4 times faster than oxygen

Mean free Path

It is the average distance a particle travels between collisions in a particular gas sample.



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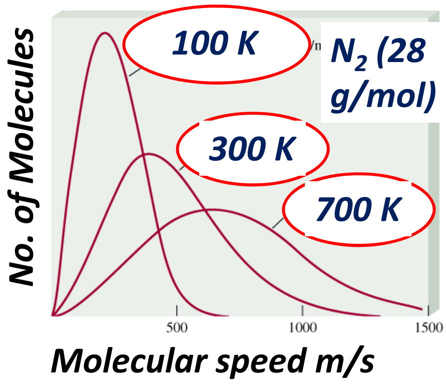
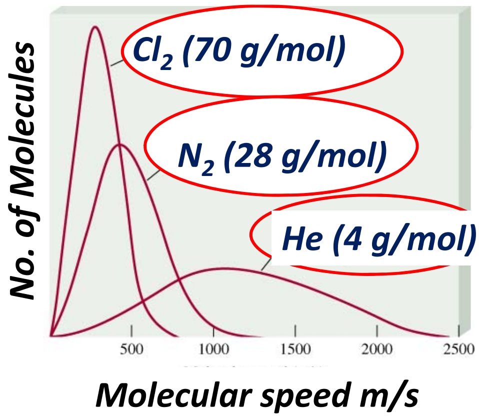


The distribution of speeds of three different gases at the same temperature T=300 K



The distribution of speeds for nitrogen gas molecules at three different temperatures

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

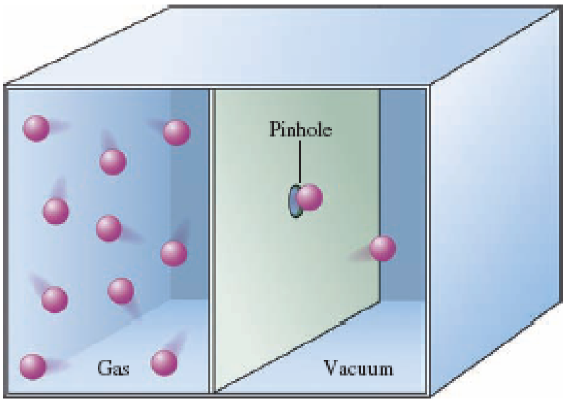
Diffusion

- A description for mixing gases.
- It also describes the movement of a gas from a region of high partial pressure to a region of lower partial pressure.
- When a small amount of ammonia is released at the front of a classroom, it takes some time before everyone in the room can smell it, because time is required for the ammonia to mix with air.
- The rate of diffusion is the rate of the mixing gases.

Effusion

is description for the passage of a gas through a tiny orifice into an evacuated chamber.

The rate of effusion measures the speed at which the gas is transferred into the chamber.



Effusion

- *Thomas Graham (1805–1869), found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles.*
- *The relative rates of effusion of two gases at the same temperature and pressure are given by the inverse ratio of the square roots of the masses of the gas particles:*

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Graham's law of effusion.

where *M_1 and M_2 represent the molar masses of the gases.*

Exercise

- *Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6), a gas used in the enrichment process to produce fuel for nuclear reactors?*

Solution

$$\frac{\text{Rate of effusion for } H_2}{\text{Rate of effusion for } UF_6} = \frac{\sqrt{M_{UF_6}}}{\sqrt{M_{H_2}}} = \frac{\sqrt{352.02}}{\sqrt{2.016}} = 13.2$$

The effusion rate of the very light H_2 molecules is about 13 times that of the massive UF_6 molecules.

KMT prediction for Graham's law of effusion

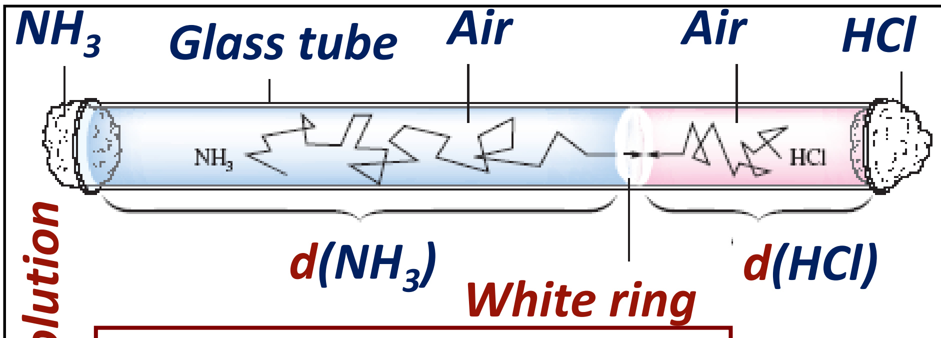
- *The effusion rate for a gas depends directly on the average velocity of its particles.*
- *The faster the gas particles are moving, the more likely they are to pass through the effusion orifice.*

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{u_{rms} \text{ for gas 1}}{u_{rms} \text{ for gas 2}} = \frac{\sqrt{\frac{3RT}{M_1}}}{\sqrt{\frac{3RT}{M_2}}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

- *Thus the kinetic molecular model does fit the experimental results for the effusion of gases.*

Exercise

- *Two cotton plugs soaked in ammonia and hydrochloric acid are simultaneously placed at the ends of a long tube. A white ring is formed inside the tube but not immediately. Guess,*
  - *What is that white ring? Write the equation?*
  - *Where do you think will the white ring appear? Which side will it be closer to?*
  - *Why does it appear after certain time not immediately?*



Solution

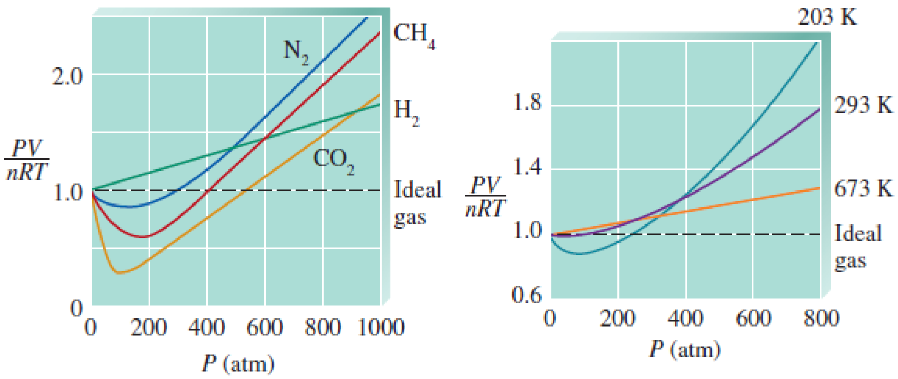
$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

ammonium chloride

$$\frac{\text{Distance traveled by } NH_3}{\text{Distance traveled by HCl}} = \frac{u_{rms(NH_3)}}{u_{rms(HCl)}} = \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}} = \frac{\sqrt{36.5}}{\sqrt{17}} = 1.5$$

The tube contains air and thus the NH_3 and HCl molecules undergo many collisions with O_2 and N_2 molecules as they travel through the tube before reaction.

Real Gases



- ***Almost all gases deviate from the ideal behavior, particularly at high pressure and low temperature.***
- ***A real gas typically exhibits behavior that is closest to ideal behavior at low pressures and high temperatures.***

Volume Correction

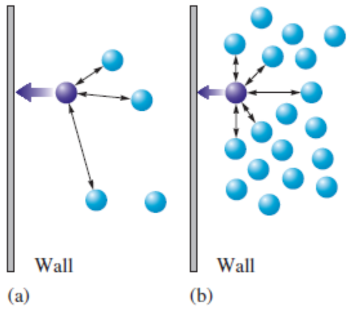
- ***The KMT assumed a zero volume for the gas molecules under any condition !!!!!!!! Wrong?***
- ***The non-zero volume of molecules implies that instead of moving in volume V they are restricted to a smaller volume V — nb, where nb is approximately the total volume taken up by the molecules themselves.***
- ***This replaces*** $p = \frac{nRT}{V} \rightarrow p' = \frac{nRT}{V - nb}$

b(molar volume) is a constant characteristic of each gas.

- ***HCl would have a slightly larger "b" correctional factor than H_2***

Pressure Correction

- The KMT assumed neither attraction nor repulsive forces (zero potential energy) between gas molecules under any condition !!!!!!!! Wrong?
  - ✓ The effect of these attractions is to make the observed pressure P_{obs} smaller than it would be if the gas particles did not interact.



$$p_{obs} = p' - \text{correction factor} = \frac{nRT}{V - nb} - \text{correction factor}$$

- The size of the correction factor depends on the molar concentration, n/V.
- The higher the concentration, the more likely a pair of gas particles will be close enough to attract each other.
- For large numbers of particles, the number of interacting pairs of particles depends on the square of the number of particles and thus on the square of the concentration, or $(n/V)^2$.

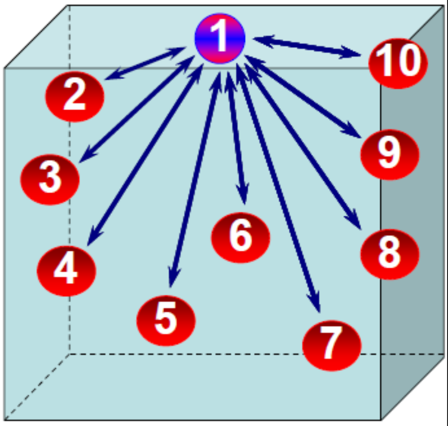
- Correction factor α frequency (number) of collisions with the walls α (n/V)
  Correction factor α force of each collision α (n/V)
  Correction factor α $(n/V)^2 = a\,(n/V)^2$

V_m (molar volume) = V/n ,
a/V^2_m is called the internal pressure of the gas

- *In a gas sample containing N particles, there is N – 1 partners available for each particle.*
- *For N particles, there are*

$$\frac{N(N-1)}{2} \textit{ pairs}$$

$$\frac{N(N-1)}{2} = \frac{10(10-1)}{2} = 45$$



- *For large N,*

$$\frac{N(N-1)}{2} \approx \frac{N^2}{2}$$

Pressure correction factor α (concentration)²

The van der Waals equation/Real gas eqn.

$$P_{obs} = \frac{nRT}{V-nb} - a\left[\frac{n}{V}\right]^2$$

$$\left[P_{obs} + \frac{an^2}{V^2}\right](V-nb) = nRT$$

$a_{(HCl)} > a_{(H2)}$ because HCl is a polar molecule and therefore has stronger intermolecular forces than H_2.

van der Waals equation corrected the KMT

Gases behave ideally at low P and high T

- ❑ *For a gas at low P (large V), $V >>> nb$,*
  $V - nb \approx V$, and the gas behaves ideally.

- ❑ *For a gas at high P (small container V), the volume of the particles becomes significant so that the volume available to the gas is significantly less than the container volume.*

At high temperatures the particles are moving so rapidly that the effects of interparticle interactions are not very important

Molar Volume at STP

- ❑ *At standard temperature and pressure, STP (1 atm and $0^{o}C$), the molar volume of ideal gases is given by*

$$V = \frac{nRT}{P} = \frac{(1.0\,mol)\left(\frac{0.08206\ L\,\text{atm}}{K\ mol}\right)(273\,K)}{1.0\,atm} = 22.4\,L$$

Gas Stoichiometry

- Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate ($CaCO_3$). Calculate the volume of CO_2 at STP produced from the decomposition of 152 g $CaCO_3$ by the reaction.

Solution

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

- Calculate the moles of $CaCO_3$ (100.9 g/mol)

$$152\,g\,CaCO_3 \times \frac{1\,mol\,CaCO_3}{100.09\,g\,CaCO_3} = 1.52\,mol\,CaCO_3$$

- The mole ratio between CO_2 and $CaCO_3$ in the balanced equation is 1:1. Hence, 1.52 moles of CO_2 will be produced. Convert from moles to volume

$$1.52\,mol\,CO_2 \times \frac{22.4\,L\,CO_2}{1\,mol\,CO_2} = 34.1\,L\,CO_2$$

Homework

- A sample of methane gas having a volume of 2.80 L at 25°C and 1.65 atm was mixed with a sample of oxygen gas having a volume of 35.0 L at 31°C and 1.25 atm. The mixture was then ignited to form carbon dioxide and water. Calculate the volume of CO_2 formed at a pressure of 2.50 atm and a temperature of 125°C. (Hint: think about the limiting reactant)

Molar Mass of a Gas/Gas density

$$n = \frac{mass\,(g)}{molar\ mass\,(g/mol)} = \frac{m}{M}$$

$$P = \frac{nRT}{V} = \frac{\left(\frac{m}{M}\right)RT}{V} = \left(\frac{m}{V}\right)\left(\frac{RT}{M}\right) = \frac{dRT}{M}$$

$$M = \frac{dRT}{P}$$

Exercise

The density of a gas was measured at 1.50 atm and 27 ℃ and found to be 1.95 g/L. Calculate the molar mass of the gas

Solution

$$M = \frac{dRT}{P}$$

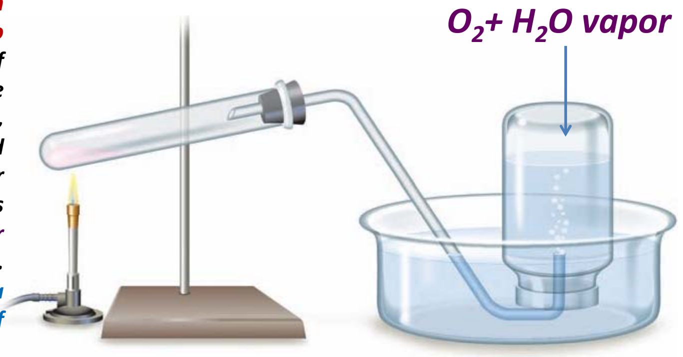
$$= \frac{\left(1.95\frac{g}{L}\right)\left(\frac{0.08206\ L\,atm}{K\ mol}\right)(300\,K)}{1.0\,atm}$$

$$= 32.0\,\frac{g}{mol}$$

Collecting a gas over water

- A mixture of gases results whenever a gas is collected by displacement of water, eg., O_2 production by thermal decomposition of $KClO_3$. MnO_2 is mixed with the $KClO_3$ to make the reaction faster.

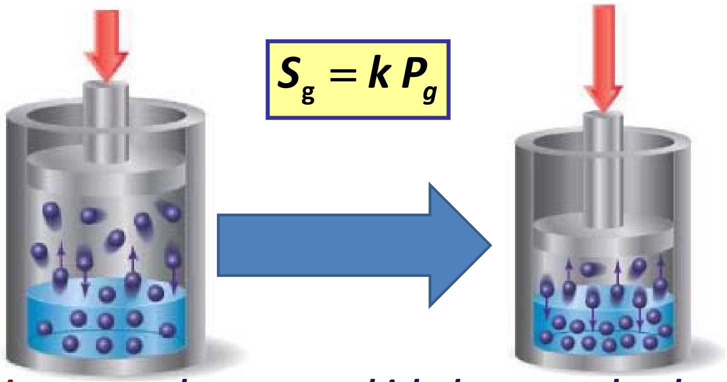
When evaporation reaches to equilibrium, (rate of evaporation = rate of condensation), the pressure exerted by the water molecules in the gas phase is called vapor pressure of water. Vapor pressure is a function of temperature



Henry's law

It states that the concentration of a gas in a solution, (S_g) is proportional to the partial pressure of this gas over the solution

$$S_g = k\,P_g$$



When P increases, the rate at which the gas molecules enter the solution increases and hence, the equilibrium concentration of the gas in solution increases

Example

- *A sample of solid potassium chlorate ($KClO_3$) was heated in a test tube and decomposed by the following reaction:*

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22°C is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of $KClO_3$ in the sample that was decomposed.

Answer

$$P_T = P_{O_2} + P_{H_2O} = P_{O_2} + 21\,torr = 754\,torr$$

Calculate P_{O2}

$$P_{O_2} = P_T - P_{H_2O} = 754\,torr - 21\,torr = 733\,torr$$

$$P_{O_2} = 733\,torr \times \frac{1\,atm}{760\,torr} = 0.964\,atm$$

Calculate n_{O2}

$$n_{O_2} = \frac{(0.964\,atm)(0.650L)}{\left(\frac{0.08206\ L\,atm}{K\ mol}\right)(295\,K)} = 2.59 \times 10^{-2}\,mol$$

The no. of moles of $KClO_3$ necessary

$$2.59\times10^{-2}\ mol\ O_2 \times \frac{2\ mol\ KClO_3}{3\ mol\ O_2} = 1.73\times10^{-2}\ mol\ KClO_3$$

The mass of $KClO_3$ (molar mass = 122.6 g/mol) in the original sample

$$1.73\times10^{-2}\ mol\ KClO_3 \times \frac{122.6\ g\ KClO_3}{1\ mol\ KClO_3} = 2.12\ g\ KClO_3$$

Exercises: ***Nitrogen trichloride gas reacts with water to form ammonia and hypochlorous acid, HOCl (aq), the main component in household bleach.***

a. *Write a balanced equation for this reaction.*
b. *How many moles of NH_3 are produced from 275 mL water (d = 1 g/mL) and excess NCl_3?*
c. *What mass of NCl_3 is required to produce 100 g ammonia?*
d. *Suppose 58 g NCl_3 and 15 g water were reacted. Which is the limiting reagent? What is the theoretical yield of ammonia and HOCl? (in moles and grams)*
e. *above: If the yield of NH_3 were only 4.4 g, what is the percent yield?*

Answer

a. $NCl_3 + 3\ H_2O \rightarrow NH_3 + 3\ HOCl$

b. *Excess NCl_3 means it is not limiting. Therefore, the mass of ammonia produced will depend only on the mass of water.*

$$\text{Mass of water} = density\ (\frac{1\,g}{mL}) \times Volume\ (275\ mL) = 275\ g$$

Equations deals only with moles or molecules

$$\text{No. of moles of water} = \frac{mass\ (275\ g)}{molar\ mass(18\ g/mol)} = 15.3\ \text{mol}$$

NCl_3	+	$3\ H_2O$	→	NH_3	+	$3\ HOCl$
		3 moles	⇨	1 moles		Stoichiometry
		15.3 moles	⇨	???? moles		

$$\text{No. of moles of } NH_3 = 15.3 \times \frac{1}{3} = 5.1\ \text{mol}$$

c. What mass of NCl_3 is required to produce 100 g ammonia?

==

This at the beginning means that water exist in excess and that NCl_3 is limiting. Therefore the mass of ammonia produced will depend only on the mass of NCl_3.

$$\text{No. of moles of } NH_3 \text{ produced} = \frac{mass\ (100\ g)}{molar\ mass\ (14 + 3\ (1) = 17\ g/mol)} = 5.88\ \text{mol}$$

NCl_3	+	$3\ H_2O$	→	NH_3	+	$3\ HOCl$
1 moles		⇨		1 moles		Stoichiometry
???? moles		⇨		5.88 moles		

$$\text{No. of moles of } NCl_3 = 5.88 \times \frac{1}{1} = 5.88\ \text{mol}$$

$$\text{Mass of } NCl_3 = No.\ of\ moles\ (5.88\ \cancel{mol}) \times molar\ mass\ (\frac{120.5g}{\cancel{mol}}) = 708.54\ g$$

d. Suppose 58 g NCl_3 and 15 g water were reacted. Which is the limiting reagent? What is the theoretical yield of ammonia and HOCl? (in moles and grams)

	NCl_3 +	$3\ H_2O$ →	NH_3 +	$3\ HOCl$
Stoichiometry	1 moles	3 moles	1 moles	3 moles
Masses	58 g	15 g	?? g	?? g
Reacted moles	0.48 moles	0.83 moles	?? moles	?? moles
Ratio	$\frac{0.48}{1} = 0.48$	$\frac{0.83}{3} = 0.28$		
Limiting Reactant	xxx	√√√	?? moles	?? moles
Rx moles	0.28 moles reacted 0.2 moles unreacted	0.83 moles	0.28 moles	0.83 moles
Th. Yield			4.7 g	43.6 g

$$\text{Percent Yield of } NH_3 = \frac{4.4}{4.7} \times 100 = 93.6\,\%$$

Homework: Phosphorus is made from reacting calcium phosphate with both silicon dioxide and elemental carbon to produce elemental phosphorus, P_4, carbon monoxide and calcium silicate, $CaSiO_3$.

a. Write the overall reaction and balance it.

b. Suppose that we reacted 500.0 g calcium phosphate with 300.0 g silicon dioxide and 100.0 g carbon. Determine the limiting reagent.

c. What mass of phosphorus is theoretically expected to be produced?

d. Suppose that the process is known to be typically 70% efficient. What mass of phosphorus can we realistically expect to get?

Exercises: *The van der Waals constants for Ar are listed below:*

Substance	a (L^2.atm mol^{-2})	b (L mol^{-1})
Ar	1.337	3.2

Using the van der Waals equation, calculate the pressures exerted by 1.00 mole of Ar gas in a 22.4 L container at 273 K. How much is the pressure deviation from ideal behavior? Which is most likely behind the deviation from ideal behavior: the volumes of the molecules or intermolecular attractions?

$$p = \frac{nRT}{V - nb} - a\left[\frac{n}{V}\right]^2$$

$$p = \frac{(1\,mol)(0.0821\,L\,atm\,mol^{-1}K^{-1})(273K)}{22.4L - \left[(1\,mol).(3.2Lmol^{-1})\right]} - 1.337\left[\frac{1\,mol}{22.4}\right]^2$$

P= 1.1674–0.00266 = 1.1648 atm

If the gas behaved ideally according to PV=nRT, P=1 atm

In the real case, the second value, 0.00266 atm, is very small, which indicates that the main cause for the tiny deviation from ideal behavior is due to the volumes of the molecules rather than intermolecular attractions.

This makes sense for the noble gas Ar that has only the very weak London dispersion forces