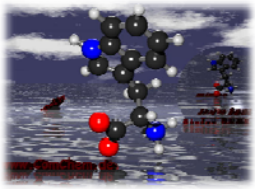
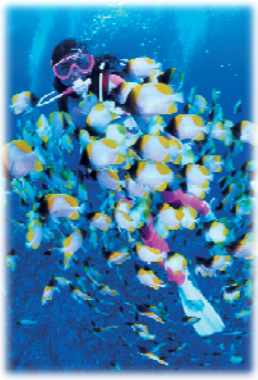
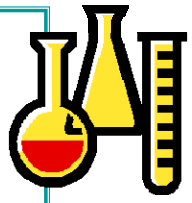




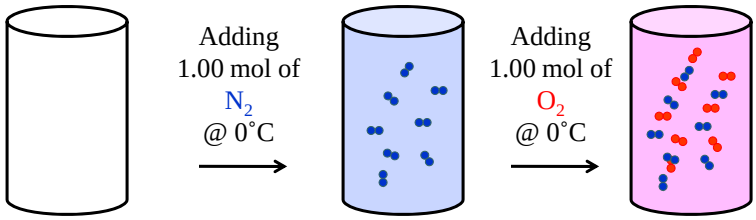
Chapter 11

Gases



Gas Mixtures

- Understanding the physical properties of gas mixtures can be attained using the ideal gas equation.

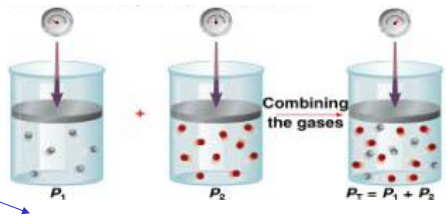


- Neither gas is affected by the presence of the other gas.
- P_{N_2} and P_{O_2} are called partial pressures.

Chapter 11 Section 5

Dalton's Law of Partial Pressures

- For a mixture of gases in a container at constant V and T, the total pressure exerted (P_{tot}) is the sum of the pressures that each gas would exert if it were alone.



P_{N_2} = 4.48 atm
P_{O_2} = 4.48 atm
P_{tot} = 8.96 atm

Partial pressures

$$P_{tot} = P_1 + P_2 + P_3 + \ldots = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \ldots$$

$$P_{tot} = (n_1 + n_2 + n_3 + \ldots)\frac{RT}{V} = \boxed{n_{tot}\left(\frac{RT}{V}\right)}$$

Chapter 11 Section 5

Applications of Dalton's Law

He: 46 L @ 25ºC and 1.0 atm

O_2: 12 L @ 25ºC and 1.0 atm

They are pumped into a 5.0 L tank @ 25ºC. Calculate P_{He}, P_{O_2} and P_{Tot}.

$$n_{He} = \frac{P V_{He}}{RT} = 1.9 \text{ mol.}$$

Similarly, $n_{O_2} = 0.49$ mol.

$$P_{He} = \frac{n_{He} RT_{He}}{V_{tank}} = 9.3 \text{ atm.} \quad \text{Also } P_{O_2} = 2.4 \text{ atm.}$$

$$P_{Tot} = P_{He} + P_{O_2} = 11.7 \text{ atm}$$

Scuba diving tanks contain mixture of helium and oxygen gases

Chapter 11 Section 5

Mole Fractions

Mole fraction of substance 1 (χ_1) $= \dfrac{n_1}{n_1 + n_2 + n_3 + \ldots}$

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

$= \dfrac{n_1}{n_{tot}}$

Also, simple derivation gives: $\chi_1 = \dfrac{P_1}{P_{tot}}$ in a given mixture.

or: $\boxed{P_1 = \chi_1 \times P_{tot}}$

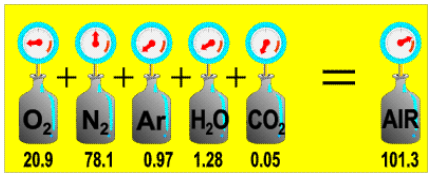
Also note that:

$$\sum_i \chi_i = 1$$

Mole fraction χ_A of each component in a mixture is directly related to its partial pressure.

Chapter 11 Section 5

Examples on Dalton's Law



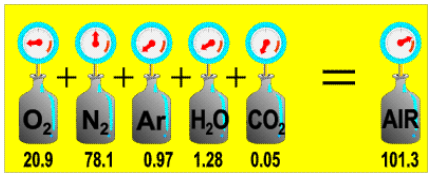
Calculate the mole fraction of oxygen in air where the values above are pressures in kPa.

$$\chi_{O_2} = \frac{P_{O_2}}{P_{air}} = \frac{20.9 \text{ kPa}}{101.3 \text{ kPa}} = 0.206$$

Also, $\boldsymbol{P_1 = \chi_1 \times P_{Tot}}$ (From the mole fraction of one component you can calculate its partial pressure)

Chapter 11 Section 5

Examples on Dalton's Law



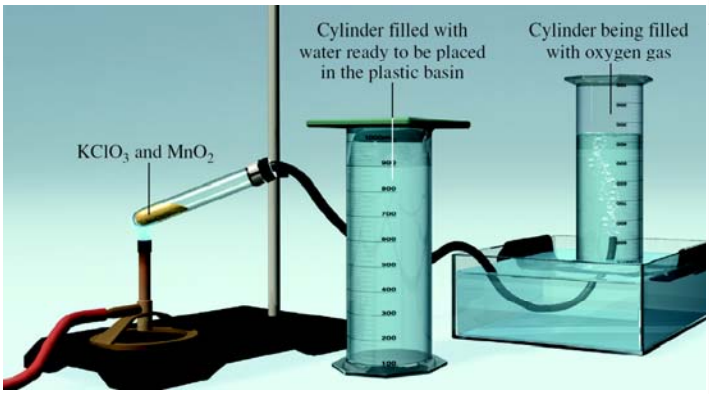
Calculate the mole fraction of oxygen in air where the values above are pressures in kPa.

$$\chi_{O_2} = \frac{P_{O_2}}{P_{air}} = \frac{20.9\ \text{kPa}}{101.3\ \text{kPa}} = 0.206$$

$P_1 = \chi_1 \times P_{Tot}$ (The partial pressure of a particular component in an ideal gaseous mixture is the mole fraction of the component times the total pressure).

Chapter 11 Section 5

Collecting a Gas Over Water



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

Table 5.3 Pressure of Water Vapor at Various Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

Chapter 11 Section 5

Collecting O_2 Gas Over Water

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

O_2 was collected @ 22ºC and P_{Tot} ($P_{O_2} + P_{H_2O}$) is 7

The volume of the gas collected is 0.650 L.

Calculate P_{O_2} and the mass of $KClO_3$ that was cons

$P_{O_2} = P_{Tot} - P_{H_2O} = 754 \text{ torr} - 21 \text{ torr} = 733 \text{ torr}.$

$$n_{O_2} = \frac{P_{O_2} V}{RT} = 2.59\times10^{-2} \text{ mol}.$$

Mass of $KClO_3$ decomposed =

$$2.59\times10^{-2} \text{ mol } O_2 \times \frac{2 \text{ mol } KClO_3}{3 \text{ mol } O_2} \times \frac{122.6 \text{ g KClO}}{1 \text{ mol KClO}}$$

Table 5.3 Pressure of Water Vapor at Various Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
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85	433.6
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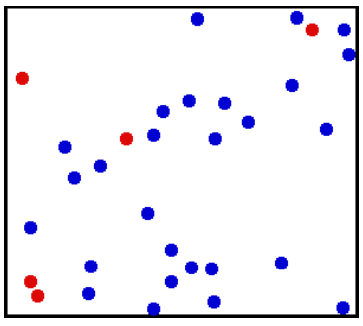
95	633.90
100	760.00

Chapter 11 Section 6

The Kinetic Molecular Theory of Gases

- Theories (or models) attempt to explain *why* physical observations (Boyle's, Charles's and Avogadro's laws) take place.
- The kinetic molecular theory (KMT) is a set of assumptions (postulates) that try to explain the behavior of ideal gas by understanding its molecular nature.



For more information about the Kinetic Molecular Theory visit: http://en.wikipedia.org/wiki/Kinetic_theory.

Chapter 11 Section 6

The Kinetic Molecular Theory of Gases

- The ***assumptions*** of KMT for **ideal** (NOT real) gases can be stated as follow:

1- A gas is composed of particles that are separated by relatively large distances. The volume occupied by individual molecules is negligible.

2- Gas molecules are constantly in random motion, moving in straight paths, colliding with the walls of their container and with one another in perfectly elastic collisions.

3- Gas particles exert no attractive or repulsive forces on one another.

4- The average kinetic energy of the particles is proportional to the absolute temperature.

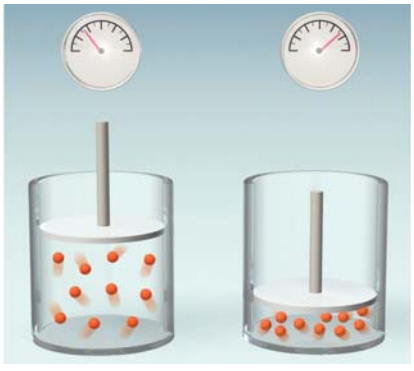
Chapter 11 Section 6

Pressure and Volume

- Boyle's law (constant n and T).
- $P = (nRT)\ \frac{1}{V}$

constant

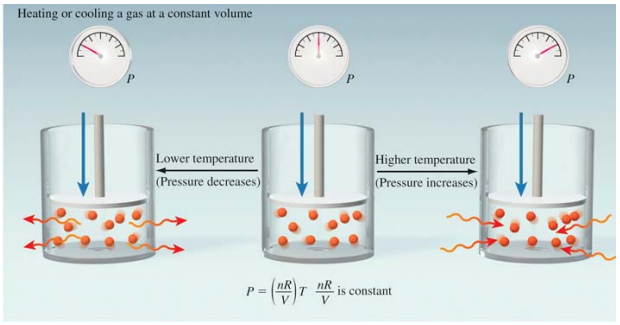
- The decrease in V means that the particles will hit the wall of the container more often, resulting in an increase of P. **(#2)**
- Gas are compressible because molecules in the gas phase are separated by large distances. **(#1)**



Chapter 11 Section 6

Pressure and Temperature

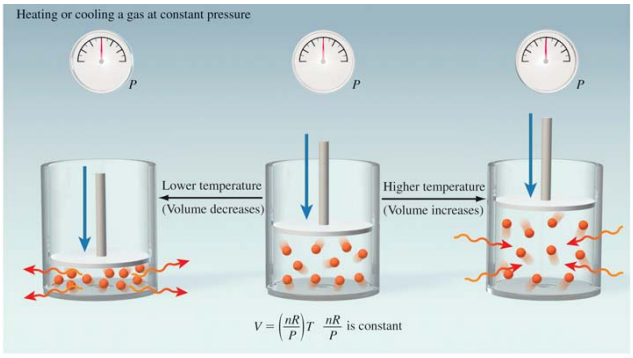
- Constant n and V.
- $P = (\frac{nR}{V})\,T$ (constant)
- When T increases, the speed of particles increases (because (#4) of the increase in KE), causing the particles to hit the wall of (#2) the container more often and with a greater force (higher P).



Chapter 11 Section 6

Volume and Temperature

- Charles's law (constant n and P).
- $V = (\frac{nR}{P})\,T$ (constant)
- When T becomes higher, the only way to keep P constant (#4) is to increase V to minimize collision forces on the wall. (#2)

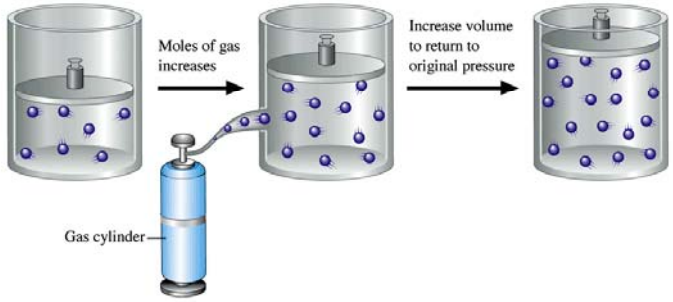


Chapter 11 Section 6

Volume and Number of Moles

- Avogadro's law (constant P and T)
- $V = (\frac{RT}{P})\, n$ (constant)
- When n increases at constant V, P would become larger. Thus, in order to keep P constant, V must be increased

(#2)

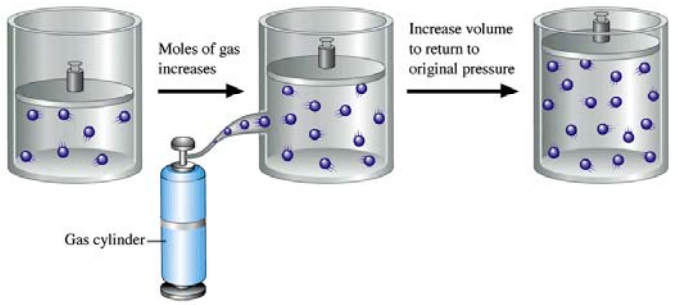


Chapter 11 Section 6

Volume and Number of Moles

- Note that the volume of a gas (at constant P and T) *depends only on the number* of gas particles present. The individual volumes of the particles are not a factor because the particle sizes are so small compared with the distances between them.

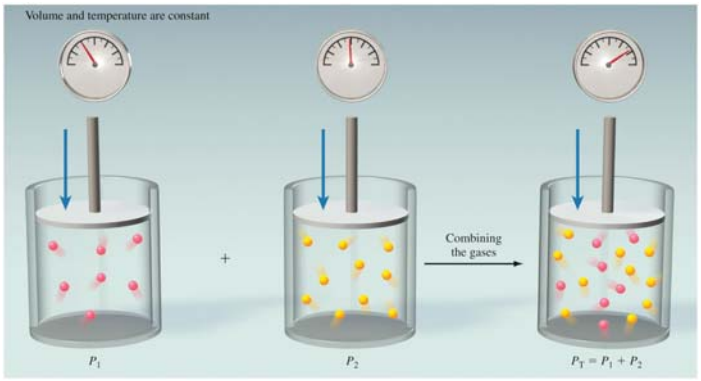
(#1)
(#3)



Chapter 11 Section 6

Mixture of Gases

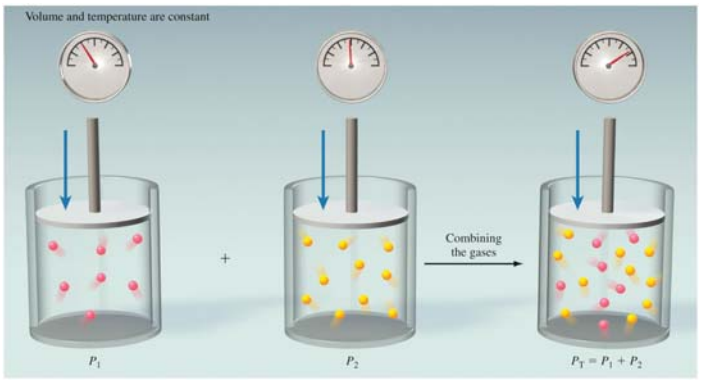
- KMT account for Dalton's law because it assumes that all gas particles are independent of each other (**#3**) and that the volumes of individual particles are not important (**#1**). Thus the identities of the gas particles are not important.



Chapter 11 Section 6

Mixture of Gases

- The Total *P* is equal to the sum of the partial *P*'s exerted by each type of particles, no matter what volumes they occupy or what kinds of particles they are.



Chapter 11 Section 6

The Meaning of Temperature

- It is important to notice that:

$$(\text{KE})_{\text{avg}} = \frac{3}{2}RT$$

  - The Kelvin temperature is an index of the random motions of gas particles.
  - The average kinetic energy of a particle *depends only* on T regardless the particle's identity.

Chapter 11 Section 6

Molecular Speed

- KMT predicts the average kinetic energy of gas molecules.

$$(\text{KE})_{\text{avg}} \text{ for one molecule} = \frac{1}{2}m\overline{u^2}$$

$$(\text{KE})_{\text{avg}} \text{ for 1 mole of particles} = N_{\text{A}}\left(\frac{1}{2}m\overline{u^2}\right)$$

(#4) $$\text{KE} = \frac{3}{2}RT \text{ (for 1 mole of any gas)}$$

N_{A} is Avogadro's number

Thus,

$$N_{\text{A}}\left(\frac{1}{2}m\overline{u^2}\right) = \frac{3}{2}RT$$

Chapter 11 Section 6

Molecular Speed

$$N_A\left(\tfrac{1}{2}m\overline{u^2}\right)=\frac{3}{2}RT$$

Average of the square of the velocity of a particle or ***mean square speed***

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

Root mean square (rms) speed

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

Because: $N_A m = M$

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

m is the mass of a particle in Kg.
N_A is 1 mole of particles.

M is the molar mass in (Kg/mol).
R = 8.314 J / K·mol

Chapter 11 Section 6

Molecular Speed

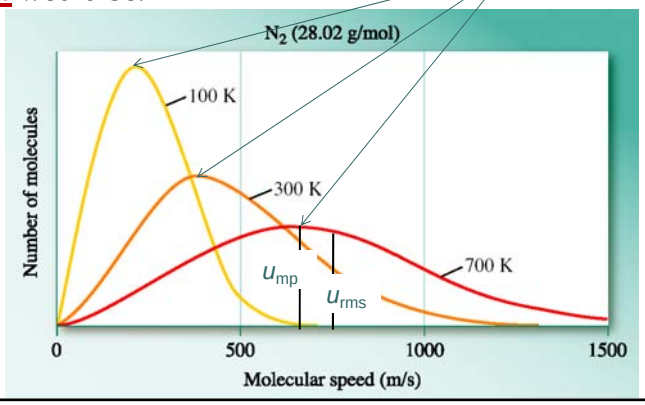
Calculate the root mean square (rms) speed for the atoms in a sample of He gas @ 25°C.

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

Chapter 11 Section 6

Effect of Temperature on Molecular Speed

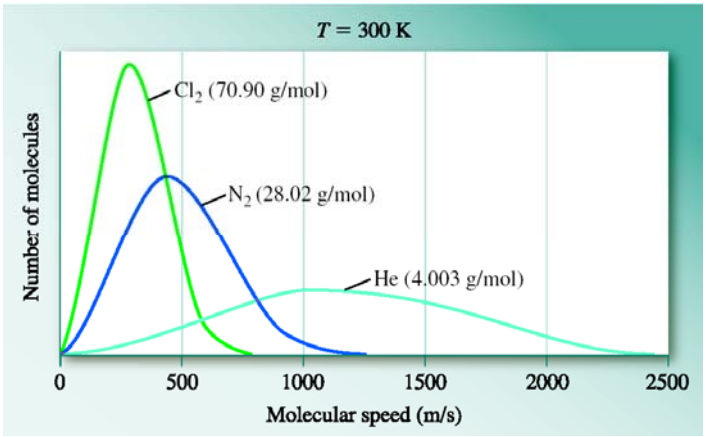
- The speed distribution curves of N_2 molecules at three different temperatures (J. Maxwell).
- The higher the temperature, the greater the ***most probable speed*** would be.



Chapter 11 Section 6

Effect of Molar Mass on Molecular Speed

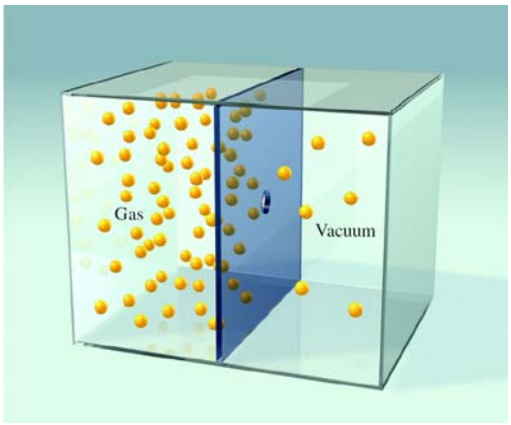
- Lighter molecules move faster than heavier ones.



Chapter 11 Section 6

Effusion

Effusion is the passage of gas particles through a pinhole to a region of vacuum.



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

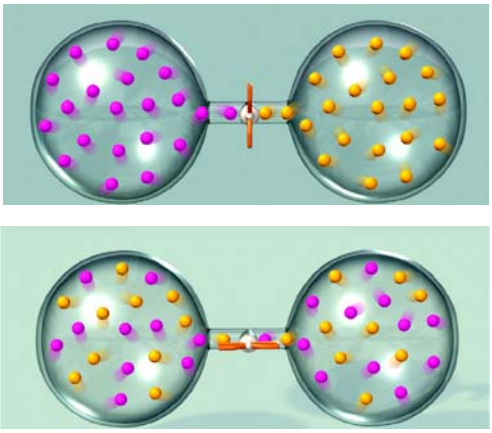
Graham's Law

$$\text{Rate} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

Chapter 11 Section 6

Diffusion

Diffusion is the process of *mixing* of gases with each other as a result of random motion and frequent collisions.



Open valve

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

Graham's Law

$$\text{Rate} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

Chapter 11 Section 6

Comparison of Molecular Speeds of Gases

- At fixed T and P, the ratio of u_{rms} of two gases can be expressed as:

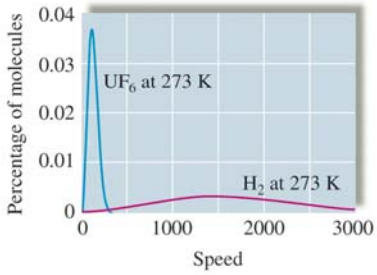
$$\frac{u_{rms}(1)}{u_{rms}(2)} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Derivation is straightforward. Check page 443

Calculate the ratio of effusion rates of H_2 and UF_6.

M_{H_2} = 2.016 g/mol.

M_{UF_6} = 352.02 g/mol.



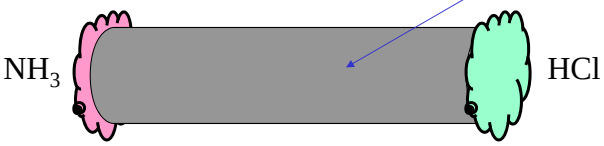
= 13.2

Chapter 11 Section 6

Application on Diffusion Rate

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

White solid (ring) forms after few minutes



- Approximation to get the diffusion rate gives:

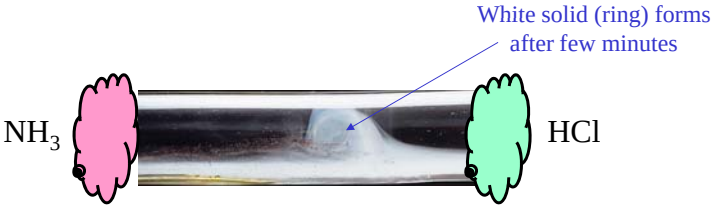
$$\frac{\text{Distance traveled by } NH_3}{\text{Distance traveled by HCl}} = \frac{u_{rms} \text{ for } NH_3}{u_{rms} \text{ for HCl}}$$

$$= \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}} = \frac{\sqrt{36.5}}{\sqrt{17}} = 1.5$$

Chapter 11 Section 6

Application on Diffusion Rate

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



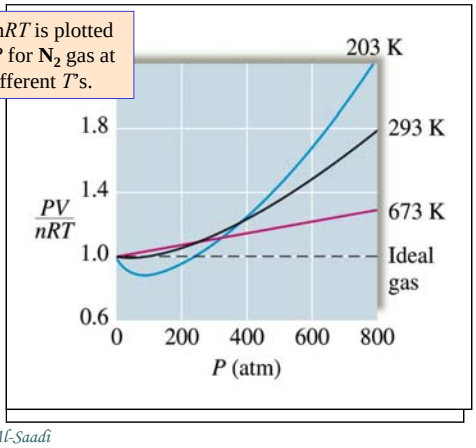
- The molecular speeds (u_{rms}) for HCl and NH_3 can be calculated at 25°C to be 450 and 660 m/s, respectively.

  So, why does it take several minutes for HCl and NH_3 to meet?

Chapter 11 Section 7

Deviation from Ideal Behavior

- No gas *exactly* follows the ideal gas law.
- Real gases deviate from ideality at **high *P*** and/or **low *T***.



Justification

For a real gas at constant *T*: *PV*/*nRT* deviates more from unity when *P* gets larger than 1 atm.

Assumption #1

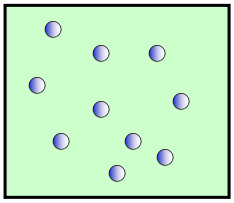
At lower *T*, real gases deviate more from ideal behavior.

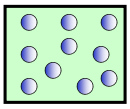
Assumption #3

Chapter 11 Section 7

Deviation from Ideal Behavior

- For very high *P*, the volume available for the gas will be significantly less than the volume of the container. The 1st assumption, subsequently, is not going to work well in this case.
- At very low *T*, the particles are moving so slow that the interparticle interactions are more significant. As a result a condensed (non-gaseous phase) will result.





Chapter 11 Section 7

The van der Waals Equation

- $PV = nRT$ describes the behavior of a hypothetical gas that:
  - has no volume (or has negligible size), and
  - its particles don't interact with each other.

  } KMT
- Johannes van der Waals made some modifications to the KMT to make the ideal gas law more applicable to real gases too.

  He suggested that the volume of gas particles are *finite*.

$$V \text{ actually available} = V \text{ (container)} - nb$$

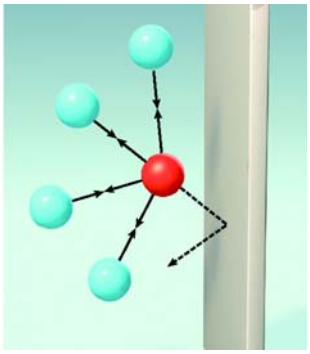
Number of moles of gas — Empirical constant

Chapter 11 Section 7

The van der Waals Equation

- Van der Waals also suggested that there are attractions taking place between the real gas particles, giving rise to P_{obs}.

$$P_{obs} < P_{ideal}$$



- The attractive force among the gas particles is directly proportional to the concentration of the gas.

  Concentration of the gas is given by n/V.

$$P_{real} = P_{ideal} - a(n/V)^2$$

$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

Chapter 11 Section 7

The van der Waals Equation

- The ideal gas equation:

$$PV = nRT$$

becomes the van der Waals equation:

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

corrected pressure term — corrected volume term

Also, a and b have specific values for each gas.

Chapter 11 Section 7

The van der Waals Equation

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

TABLE 11.6 Van der Waals Constants of Some Common Gases

Gas	$a\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$	Gas	$a\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237	O_2	1.36	0.0318
Ne	0.211	0.0171	Cl_2	6.49	0.0562
Ar	1.34	0.0322	CO_2	3.59	0.0427
Kr	2.32	0.0398	CH_4	2.25	0.0428
Xe	4.19	0.0510	CCl_4	20.4	0.138
H_2	0.244	0.0266	NH_3	4.17	0.0371
N_2	1.39	0.0391	H_2O	5.46	0.0305