Chemistry 331

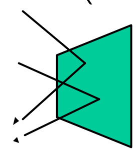
Lecture 9
Ideal Gas Behavior

NC State University

Macroscopic variables P, T

Pressure is a force per unit area (P= F/A)

The force arises from the change in momentum as particles hit an object and change direction.



Temperature derives from molecular motion (3/2RT = 1/2M<u²>) M is molar mass

Greater average velocity results in a higher temperature.

u is the velocity

Mass and molar mass

We can multiply the equation:

$$\frac{3}{2}RT = \frac{1}{2}M <u^2>$$

by the number of moles, n, to obtain:

$$\frac{3}{2}nRT = \frac{1}{2}nM <u^2>$$

If m is the mass and M is the molar of a particle then we can also write:

nM = Nm (N is the number of particles)

Mass and molar mass

In other words nN_A = N where N_A is Avagadro's number.

$$\frac{3}{2}nRT = \frac{1}{2}Nm <u^2>$$

Kinetic Model of Gases

Assumptions:
1. A gas consists of molecules that move randomly.
2. The size of the molecules is negligible.
3. There are no interactions between the gas molecules.

Because there are such large numbers of gas molecules in any system we will interested in average quantities.

We have written average with an angle bracket. For example, the average speed is:

$$<u^2> = c^2 = \left(\frac{s_1^2 + s_2^2 + s_3^2 + \ldots + s_N^2}{N}\right)$$

$$\bar{c} = \left(\frac{s_1 + s_2 + s_3 + \ldots + s_N}{N}\right)$$

We use s for speed and c for mean speed.

Velocity and Speed

When we considered the derivation of pressure using a kinetic model we used the fact that the gas exchanges momentum with the wall of the container. Therefore, the vector (directional) quantity velocity was appropriate. However, in the energy expression the velocity enters as the square and so the sign of the velocity does not matter. In essence it is the average speed that is relevant for the energy. Another way to say this is the energy is a scalar.

$$E = \frac{1}{2}m<u^2> = \frac{1}{2}mv^2 = \frac{1}{2}mc^2$$

$$p = m\mathbf{u} = mv$$

All of these notations mean the same thing.

The root-mean-square speed

The ideal gas equation of state is consistent with an interpretation of temperature as proportional to the kinetic energy of a gas.

$$\frac{1}{3}M\left\langle u^2\right\rangle = RT$$

If we solve for <u²> we have the mean-square speed.

$$\langle u^2\rangle = \frac{3RT}{M}$$

If we take the square root of both sides we have the r.m.s. speed.

$$\left\langle u^2\right\rangle^{1/2} = \sqrt{\frac{3RT}{M}}$$

The mean speed

The mean value is more commonly used than the root-mean-square of a value. The root-mean-square speed Is equal to the root-mean-square velocity:

$$c^2 = \langle u^2\rangle$$

The mean speed is:

$$\bar{c} = \sqrt{\frac{8}{3\pi}c^2}$$

The r.m.s. speed of oxygen at 25 ºC (298 K) is 482 m/s.
Note: M is converted to kg/mol!

$$\langle u^2\rangle^{1/2} = \sqrt{\frac{3(8.31\,J/mol\text{-}K)(298K)}{0.032\,kg/mol}} = 481.8\ m/s$$

The Maxwell Distribution

Not all molecules have the same speed. Maxwell assumed that the distribution of speeds was Gaussian.

$$F(s) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} s^2 \exp\left\{-\frac{Ms^2}{RT}\right\}$$

As temperature increases the r.m.s. speed increases and the width of the distribution increases. Moreover, the fucntions is a normalized distribution. This just means that the integral over the distribution function is equal to 1.

$$\int_0^\infty F(s)ds = 1$$

See the MAPLE worksheets for examples.

Diffusion and Effusion

Diffusion: process by which substances mix with one another
Effusion: escape of a gas through a small hole

Graham's law of effusion:

$$\textit{Rate of effusion} \propto \frac{1}{\sqrt{M}}$$

Can be related to the r.m.s. speed of a gas given by the kinetic theory of gases.

Molecular Collisions

The mean free path, λ is the average distance that a molecule travels between collisions.
The collision frequency, z is the average rate of collisions made by one molecule.
The collision cross section, σ is target area presented by one molecule to another.
When interpreted in the kinetic model it can be shown that:

$$\lambda = \frac{RT}{\sqrt{2}N_A\sigma P}\ ,\ z = \frac{\sqrt{2}N_A\sigma\sqrt{\langle u^2\rangle}P}{RT}\ ,\ \sigma = \pi d^2$$

In other words:

$$\sqrt{\langle u^2\rangle} = \lambda z$$

Units of Pressure

Force has units of Newtons

F = ma (kg m/s²)

Pressure has units of Newtons/meter²

P= F/A = (kg m/s²/m² = kg/s²/m)

These units are also called Pascals (Pa).

1 bar = 10^5 Pa = 10^5 N/m².

1 atm = 1.01325 x 10^5 Pa

Units of Energy

Energy has units of Joules

1 J = 1 Nm

Work and energy have the same units.

Work is defined as the result of a force acting through a distance.

We can also define chemical energy in terms of the energy per mole.

1 kJ/mol

1 kcal/mol = 4.184 kJ/mol

Thermal Energy

Thermal energy can be defined as RT.

Its magnitude depends on temperature.

R = 8.31 J/mol-K or 1.98 cal/mol-K

At 298 K, RT = 2476 J/mol (2.476 kJ/mol)

Thermal energy can also be expressed on a per molecule basis. The molecular equivalent of R is the Boltzmann constant, k.

$R = N_A k$

$N_A = 6.022 \times 10^{23}$ molecules/mol

Extensive and Intensive Variables

Extensive variables are proportional to the size of the system.

Intensive variables do not depend on the size of the system.

Extensive variables: volume, mass, energy

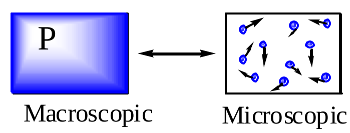
Intensive variables: pressure, temperature, density

Equation of state relates P, V and T

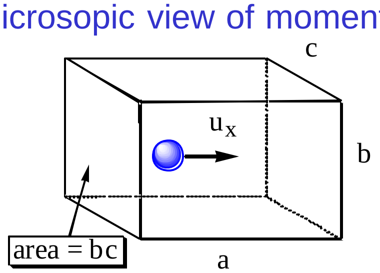
The ideal gas equation of state is

$PV = nRT$

An equation of state relates macroscopic properties which result from the average behavior of a large number of particles.



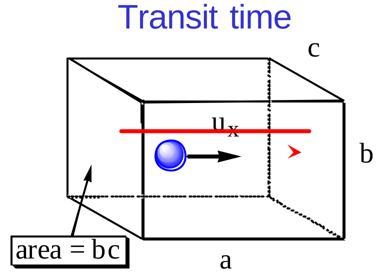
Microsopic view of momentum



A particle with velocity u_x strikes a wall.

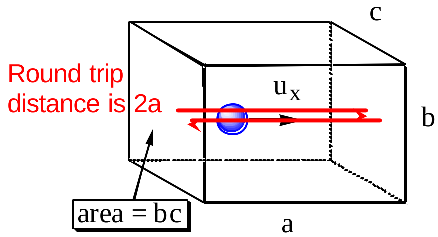
The momentum of the particle changes from mu_x to $-mu_x$. The momentum change is $\Delta p = 2mu_x$.

Transit time



The time between collision is $\Delta t = 2a/u_x$.

Transit time



The time between collision is $\Delta t = 2a/u_x$.
velocity = distance/time.
time = distance/velocity.

The pressure on the wall

force = rate of change of momentum

$$F = \frac{\Delta p}{\Delta t} = \frac{2mu_x}{2a/u_x} = \frac{mu_x^2}{a}$$

The pressure is the force per unit area.
The area is A = bc and the
volume of the box is V = abc

$$P = \frac{F}{bc} = \frac{mu_x^2}{abc} = \frac{mu_x^2}{V}$$

Average properties

Pressure does not result from a single particle striking the wall but from many particles. Thus, the velocity is the average velocity times the number of particles.

$$P = \frac{Nm\langle u_x^2 \rangle}{V}$$

$$PV = Nm\langle u_x^2 \rangle$$

Average properties

There are three dimensions so the velocity along the x-direction is 1/3 the total.

$$\langle u_x^2 \rangle = \frac{1}{3}\langle u^2 \rangle$$

$$PV = \frac{Nm\langle u^2 \rangle}{3}$$

From the kinetic theory of gases

$$\frac{1}{2}Nm\langle u^2 \rangle = \frac{3}{2}nRT$$

Putting the results together

When we combine of microscopic view of pressure with the kinetic theory of gases result we find the ideal gas law.

$$PV = nRT$$

This approach applies to a monatomic gas like neon or argon. What about internal motions of molecules?

RT is a natural energy scale

We can rewrite the ideal gas law in terms of the molar volume

$$\bar{V} = V/n$$

The ideal gas law has the form

$$P\bar{V} = RT$$

The molar volume at standard T and P

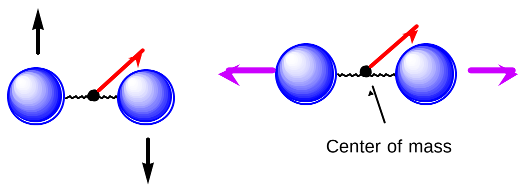
$$\bar{V} = \frac{RT}{P} = \frac{(8.31\ J/mol\text{–}K)(298\ K)}{(1.013 \times 10^5\ N/m^2)} = 0.0244\ m^3 = 24.4\ L$$

Microscopic variables

Monatomic gases: translation

Pressure and temperature can be described solely in terms of the ballistic motion of the gas.

Diatomic gases: translation, vibration, rotation



Quantized energy levels

The constant h, known as Planck's constant gives the scale for quantized energy levels.

$h = 6.626 \times 10^{-34}$ J

Translation – particle in a box

Vibration – harmonic oscillator

Rotation – rigid rotator

The energy levels for each of these is obtained by solution of the Schrödinger equation.

The energy level spacing

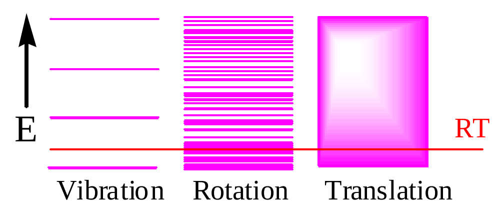
The constant h, known as Planck's constant gives the scale for quantized energy levels.

$h = 6.626 \times 10^{-34}$ J

Motion	#	Formula	kJ/mol
Vibration	v	$(v + 1/2)h\nu$	1 – 20
Rotation	J	$[h^2/8\pi^2 I]J(J+1)$	$10^{-3} – 1$
Translation	n	$[h^2/8ma^2]n^2$	10^{-11}

We will see how to obtain these in the second half of the course.

Levels are thermally populated



Key points regarding the microscopic view

Translational energy levels are so densely spaced that these can be treated using classical methods.

We can treat particles as ideal even though they have vibrations and rotations. The dynamics of the gas are not affected.

We will see that the heat capacity of the gas is affected by the "internal" degrees of freedom.

Key points regarding the microscopic view

The kinetic energy of a large number of individual particles is proportional to the temperature of the system. As the system heats up we can picture the molecules moving more rapidly.

Pressure results from the net momentum transfer between the particles and wall of the container.

Pressure of a dense fluid

For a dense fluid (or a liquid) such as water we can think of the pressure arising from the weight of the column of fluid above the point where the measurement is made.

The force is due to the mass of water m (kg) accelerated by gravity ($g = 9.8\ m/s^2$).

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{mgh}{Ah} = \frac{mgh}{V} = \rho gh$$

where ρ is the density $\rho = m/V$.

The dependence of atomspheric pressure on altitude

We can think of the atmosphere is a fluid, but it is not dense. Moreover, unlike water the density of the atmosphere decreases with altitude. Thus, at high elevations both the pressure and the density are decreased. To obtain the dependence of pressure on height h above the earth's surface we use the ideal gas law to define the density of an ideal gas.

The dependence of atomspheric pressure on altitude

The density of an ideal gas is:

$\rho = m/V = nM/V = MP/RT$

The dependence of pressure on elevation is:

$$dP = -\rho g\,dh = -\frac{MPg}{RT}dh$$

We need to collect variables of integration on the same side of the equation.

$$\frac{dP}{P} = -\frac{Mg}{RT}dh$$

The barometric pressure formula

Then we integrate (assuming P_0=1 at h=0):

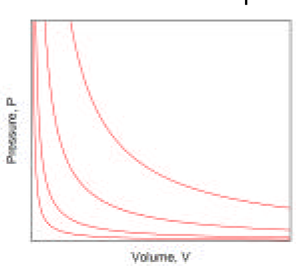
$$\int_{P_0=1}^{P} \frac{dP}{P} = -\frac{Mg}{RT}\int_0^h dh$$

$$\ln\left(\frac{P}{P_0}\right) = -\frac{Mgh}{RT}$$

$$P = P_0 \exp\left\{-\frac{Mgh}{RT}\right\} \text{ or } P = \exp\left\{-\frac{Mgh}{RT}\right\} \text{ atm}$$

Isotherms

We can plot the pressure as a function of the volume as shown below. Each of the curves on the plot has a constant temperature.



Partial pressure

For any gas in a mixture of gases the partial pressure is defined as:

$P_j = x_j P$

where x_j is the mole fraction of component j and P is the total pressure.

The mole fraction is defined as:

$$x_j = \frac{n_j}{\sum_i n_i}$$