

Chemistry 331

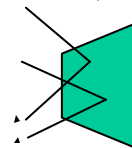
Lecture 2 Ideal Gas Behavior

NC State University

Macroscopic variables P, T

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

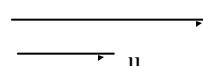
The force arises from the change in momentum as particles hit an object and change direction.



Temperature derives from molecular motion ($3/2RT = 1/2Mu^2$)

M is molar mass

Greater average velocity results in a higher temperature.



Units of Pressure

Force has units of Newtons

$$F = ma \text{ (kg m/s}^2\text{)}$$

Pressure has units of Newtons/meter²

$$P = F/A = (\text{kg m/s}^2/\text{m}^2 = \text{kg/s}^2/\text{m})$$

These units are also called Pascals (Pa).

$$1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ N/m}^2.$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

Units of Energy

Energy has units of Joules

$$1 \text{ J} = 1 \text{ Nm}$$

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.

$$1 \text{ kJ/mol}$$

$$1 \text{ kcal/mol} = 4.184 \text{ kJ/mol}$$

Thermal Energy

Thermal energy can be defined as RT .

Its magnitude depends on temperature.

$$R = 8.31 \text{ J/mol-K} \text{ or } 1.98 \text{ cal/mol-K}$$

$$\text{At } 298 \text{ K, } RT = 2476 \text{ J/mol (2.476 kJ/mol)}$$

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

$$R = N_A k$$

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

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.

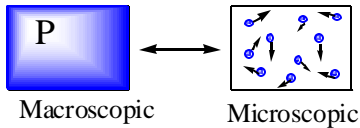
Extensive variables: volume, mass, energy
Intensive variables: pressure, temperature, density

Equation of state relates P, V and T

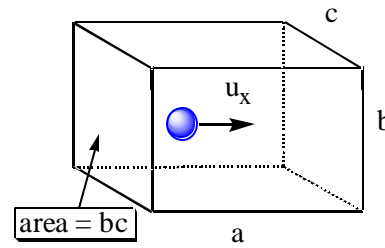
The ideal gas equation of state is

$$PV = nRT$$

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

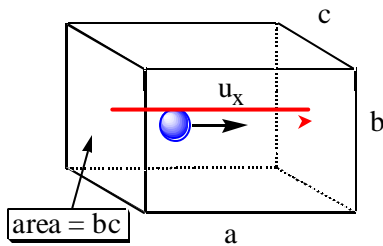


Microscopic view of momentum



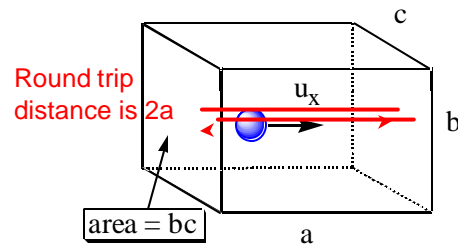
A particle with velocity u_x strikes a wall. The momentum of the particle changes from mu_x to $-mu_x$. The momentum change is $\Delta p = 2mu_x$.

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

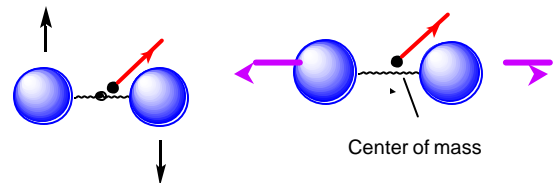
$$\bar{v} = \frac{RT}{P} = \frac{(8.31 \text{ J/mol-K})(298 \text{ K})}{(1.013 \times 10^5 \text{ N/m}^2)} = 0.0244 \text{ m}^3 = 24.4 \text{ L}$$

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.

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

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

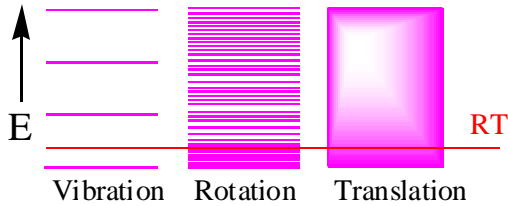
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Motion	#	Formula	kJ/mol
Vibration	v	$(v + 1/2)h\nu$	~ 20
Rotation	J	$[h^2/8\pi^2I]J(J+1)$	$10^{-3} - 1$
Translation	n	$[h^2/8ma^2]n^2$	10^{-11}

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 ($g = 9.8 \text{ m/s}^2$).

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

where ρ is the density $\rho = m/V$.

The dependence of atmospheric pressure on altitude

We can think of the atmosphere as 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 atmospheric pressure on altitude

The density of an ideal gas is:

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

The dependence of pressure on elevation is:

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

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

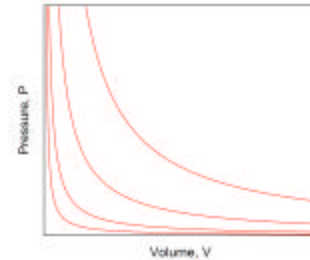
Then we integrate (assuming $P=1$ at $h=0$):

$$\int_1^P \frac{dP}{P} =$$

(-)

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:

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