Thermodynamics: a microscopic view

Mole and Avogadro's Number

One <u>mole</u> of a substance contains 6.022×10^{23} atoms or molecules that make up the substance. The number 6.022×10^{23} is known as <u>Avogadro's number</u>, N_A. It follows that

$$\text{No. of moles, } n = \frac{N}{N_A}$$

where N is the no. of atoms or molecules.

Ideal Gas

An <u>ideal gas</u> is an idealized model for real gases that have sufficiently low densities.

The condition of low density means that the molecules are so far apart that they do not interact except during collisions, which are effectively elastic.

Simulation

The Ideal Gas Law

The ideal gas law states that:

$$PV = nRT$$

where P is pressure, V is volume, n is the number of moles, T is the absolute temperature, and <u>R = 8.31 J/(mol K) is the universal gas constant.</u>

The ideal gas law can be written in terms of N, the number of molecules instead.

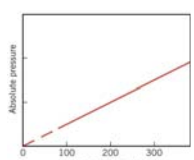
$N = n N_A$, so: $PV = nN_A \frac{R}{N_A} T = NkT$

where <u>$k = R/N_A$ = 1.38×10^{-23} J/K is the Boltzmann constant.</u>

The Ideal Gas Law

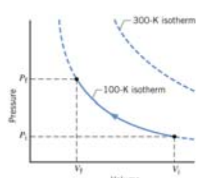
At constant volume, the pressure is proportional to the temperature.

$$P \propto T$$



At constant temperature, the pressure is inversely proportional to the volume.

$$P \propto 1/V$$



The pressure is also proportional to the amount of gas.

$$P \propto n$$

Raising the temperature

The temperature of an ideal gas is raised from 10°C to 20°C while the volume is kept constant. If the pressure at 10°C is P, what is P_f, the pressure at 20°C?

1. $P_f < P$
2. $P_f = P$
3. $P < P_f < 2P$
4. $P_f = 2P$
5. $P_f > 2P$

Raising the temperature

This is a situation in which we're using an equation (the ideal gas law) involving the temperature T, so T should be in Kelvin.

The temperature of an ideal gas is raised from 283K to 293K while the volume is kept constant. If the pressure at 283K is P, what is P_f, the pressure at 293K?

Not much more than *P.*

Kinetic theory

Kinetic theory is the application of Newton's Laws to ideal gases. Start with one atom of ideal gas in a box and determine the pressure associated with that atom at a given temperature. Then add more atoms and average over all the atoms.

Results from kinetic theory, 1

1. Pressure is associated with collisions of gas particles with the walls. Dividing the total average force from all the particles by the wall area gives the pressure.

Increasing temperature increases pressure for two reasons. First, there are more collisions. And secondly, because the particles move faster at higher temperatures, the collisions involve a larger average impact force.

For a fixed volume and temperature, adding more particles increases pressure because there are more collisions.

Results from kinetic theory, 2

2. The average translational kinetic energy for **each molecule** is:

$$K_{\text{translation}} = \frac{3}{2}kT$$

where $K_{\text{translation}} = ½\, m v_{rms}^2$

By definition, $v_{rms}^2 = \langle v^2 \rangle$, *and* v_{rms} is called the root mean square velocity.

Internal Energy of Ideal Gases and the number of degrees of freedoms

For a general ideal, the internal energy per molecule is its total kinetic energy:

$$U = K_{\text{translation}} + K \text{ due to other motions}$$

$$U = (3 + n_f)kT/2.$$

Where n_f is the number of degrees of freedom other than translation.

Internal Energy of Ideal Gases and the number of degrees of freedoms

Recall that the internal energy of a system is the energy associated with the motion of atoms and/or molecules. In general, the motion of a molecule is consisted of translations, rotations and vibrations. How many different kinds of motions a molecule can perform depends on how complicated the structure of the molecule is. In general, the more complicated the structure is the more number of kinds of motions can take place. We call each kind of motion a degree of freedom. Note that three degrees of freedom are counted for translational motions, with translations in each of the x, y and z directions counted as one degree of freedom.

Internal Energy of Ideal Gases and the number of degrees of freedoms

Thermodynamics tell us that for a system at equilibrium, each degree of freedom acquires an average energy of $kT/2$ per molecule. So, for translational motions alone, the component of internal energy they account for is $3kT/2$ per molecule as quoted earlier.

For monatomic ideal gases, the only kind of motions possible is translational motion. So, their internal energy is: $U = 3kT/2$ per molecule.

For diatomic ideal gases, it can have two additional degrees of freedom (coming from rotation). So, their internal energy is:

$U = 5kT/2$ per molecule.

(Note that if temperature is high enough, vibrational motions may be excited and the expression for the internal energy may change.)

Light and heavy atoms

A box of ideal gas consisting of both light and heavy particles (the heavy ones have 16 times the mass of the light ones). Initially all the particles have the same speed. When equilibrium is reached, what can we say about the ratio of their rms speed?

Solution:

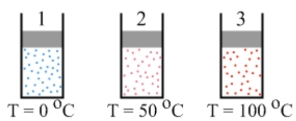
By the kinetic theory, $\frac{1}{2} m v_{rms}^2 = 3/2(kT)$.

At equilibrium, the two kinds of particles have the same temperature. It follows that

$m_L v_{rms,L}^2 = m_H v_{rms,H}^2 \Rightarrow v_{rms,L}/v_{rms,H} = \sqrt{(m_H/m_L)} = 4$

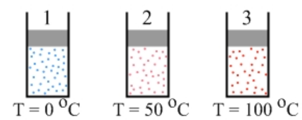
Three Cylinders

Three identical cylinders are sealed with identical pistons that are free to slide up and down the cylinder without friction. Each cylinder contains an ideal gas that occupies the same volume, but the temperature is different in each case, equal to 0, 50 and 100ºC, respectively. The other side of the piston covering the cylinders is exposed to the atmosphere. How do the pressures of the gases compare?

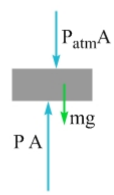


1. 1>2>3
2. 3>2>1
3. all equal
4. not enough information to say

Three Cylinders



Free-body diagram of one of the pistons:



$P = P_{atm} + mg/A$

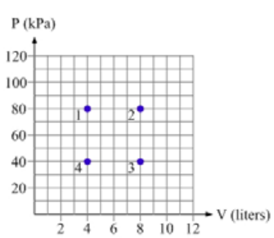
This shows that all three pistons have the same pressure. And, because $n = PV/RT$, the number of moles of gas must be in the order 1 > 2 > 3.

P-V Diagram

P-V (pressure versus volume) diagrams can be very useful.

What are the units resulting from multiplying pressure in kPa by volume in liters?

$$1000\frac{\text{N}}{\text{m}} \times 0.001\,\text{m}^3 = 1\,\text{Nm} = 1\,\text{J}$$



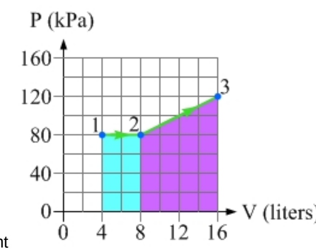
Question: Rank the four states shown on the diagram based on their absolute temperature, from greatest to least.

Answer: Temperature is proportional to PV, so rank by PV:

2 > 1=3 > 4.

Work: Area under the P-V Curve

$$W = \underbrace{PA}_{\text{Force}}\underbrace{\Delta x}_{\text{Displacement}} = P\Delta V$$



The net work done by the gas is positive in this case, because the change in volume is positive, and equal to the area under the curve.

Work: Area under the P-V Curve

What will be the work done by the gas if the direction of change in volume is reversed?

Since $W = P\Delta V$, if the sign of ΔV is reversed, the sign of W is reversed. For the example shown in the previous page, the work done by the gas would be negative. That means work is done to the gas to decrease its volume.

Isotherms

Isotherms are lines of constant temperature.

On a P V diagram, isotherms satisfy the equation:

PV = constant