

## Energy IV: Chemical Energy

### 1: The form of heat energy

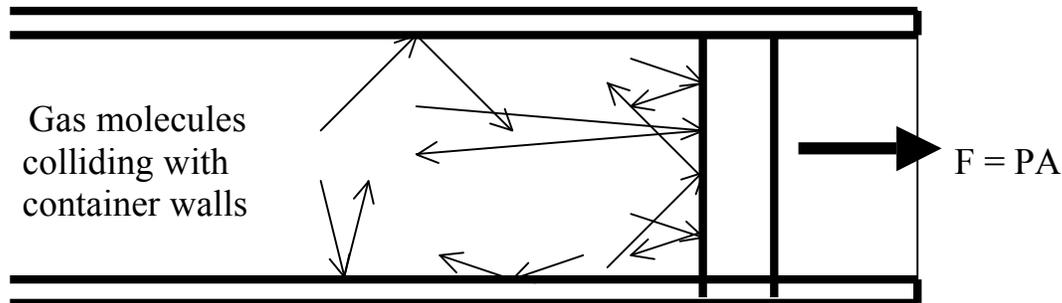
Now that we have seen some of the work and ideas that went into establishing that heat is a form of energy, a natural follow up question is just *what* form of energy is it? More precisely, what is the form of the *internal energy* of a system that can be modified by heat or work? The answer to this question was obtained in the mid to late 19<sup>th</sup> century by the three physicists, Maxwell of Scotland, Boltzmann of Austria and Gibbs of America. It turns out that the answer depends fundamentally on the conception of matter as consisting of very large numbers of very small particles that we call **atoms** and **molecules**. The early evidence for this particulate makeup of matter, aside from the fact that it has been an appealing idea to many people from very ancient times, came primarily from two sources in early chemistry.

First, the precise measurements of the masses of substances participating in chemical reactions and the discovery of the **conservation of mass** in such reactions by Lavoisier in the eighteenth century. Second, the discovery, by Dalton in the early nineteenth century, of simple combining ratios of masses of distinct chemical substances participating in chemical reactions. For example, the forming of water vapor from hydrogen and oxygen always involves consuming 16 gm of oxygen and 2 gm of hydrogen for every 18 gm of water produced.. These results are easily understood if definite numbers of molecules with fixed masses and undergoing rearrangements of their constituent atoms are the basic ingredients of chemical reactions.

Combining observations like this for many different reactions (a process of chemical analysis that proceeded over two centuries) one eventually determines the composition of the molecules of various substances in terms of the atoms of the **chemical elements** or basic substances. Thus the water molecule is H<sub>2</sub>O, i.e., a composite of two hydrogen atoms (H) and one oxygen atom (O) and the oxygen atom is 16 times as massive as the hydrogen atom. This makes the water molecule 18 times as massive as the hydrogen atom.

This atomistic conception of matter also leads to a mechanical understanding of many of the macroscopic properties of matter. Thus the pressure of confined gasses is understood as a result of the myriad collisions of the

individual molecules that make up the gas with the walls of the confining vessel (**Fig. 1**).



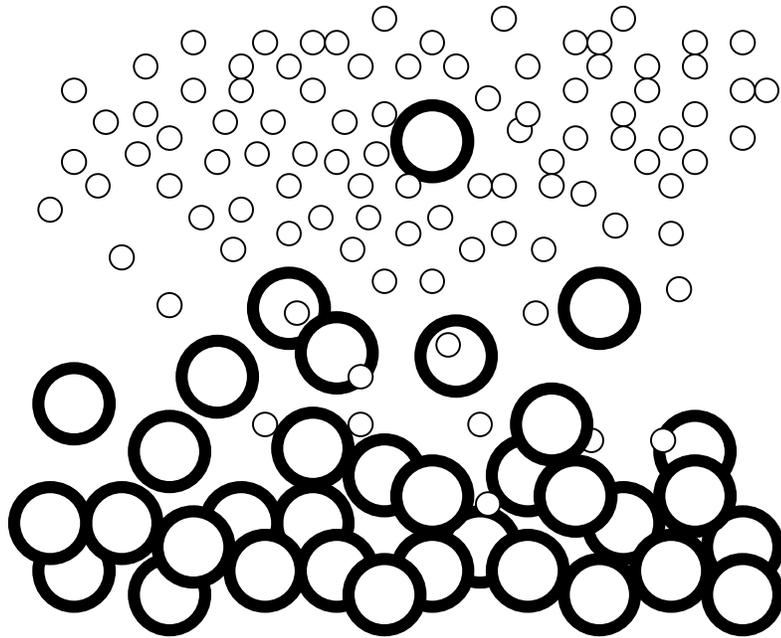
**Fig. 1:** Pressure generated by molecular collisions with container walls.

For ‘ordinary’ quantities of gas the number of molecules is *very* large and they are moving largely as free particles in all directions except when they collide with each other or the walls. Similarly, the mixing of distinct gasses or liquids by the comparatively slow process of **diffusion** is understood as a consequence of the motion of individual molecules of each substance gradually meandering, via collisions, from separated regions of relatively pure concentration to neighboring regions of increasingly mixed concentrations (**Fig. 2**).

The elastic properties of solids is understood as the result of a geometrical distortion of shape (**strain**) altering the tiny distances between neighboring molecules and thereby giving rise to restoring forces (**stress**) that, for modest distortions, are, like springs, proportional to the strain.

In general the properties of gasses and solids are easier to explain than liquids because gas molecules have almost no external forces acting on them most of the time while molecules in solids move only very small distances relative to one another. Liquids are intermediate between gases and solids and their molecules, often joined together into small molecular clumps, can move through large relative distances while subject to significant forces.

In all the phases of matter, however, there is no way of keeping track of the detailed motion of any given molecule or atom in a macroscopic sample and the only kind of analysis of molecular/atomic motion that is feasible is a



**Fig. 2:** Distinct molecular types diffusing from regions of high concentration into regions of lower concentration.

*statistical analysis* in which we try to determine the *average values* of speed or kinetic energy or distance between consecutive collisions or frequency of collisions or distance between neighboring molecules, etc. Often, if the analysis is pressed hard enough, one can calculate the probabilities that these various quantities have values lying within specified intervals and one may even be able to test the calculations by measuring the statistical distribution of these values.

As an example consider the ideal gas law that we discussed in the previous class,

$$P V = M \kappa T, \quad (1.1)$$

and which gasses satisfy if the pressure isn't too high nor the temperature too low. By comparing the gasses of oxygen, hydrogen, water vapor, carbon monoxide and carbon dioxide, etc., we find that *equal multiples* of 32 gm of oxygen or 2gm of hydrogen or 18gm of water vapor or 28gm of carbon monoxide or 44gm of carbon dioxide, etc., all have the same value of the ratio,

$$P V / T =$$

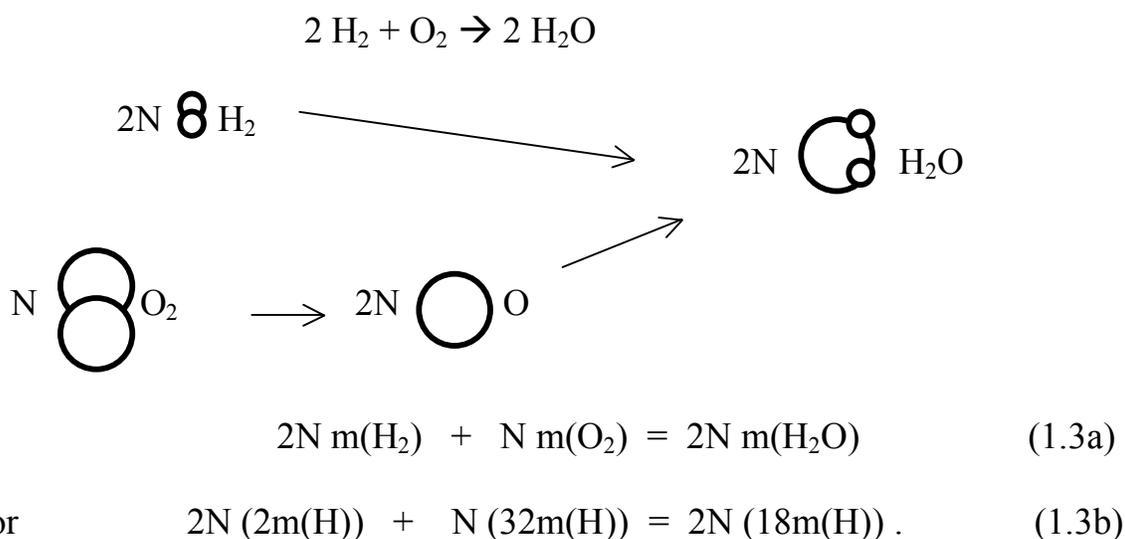
$$n_{\text{mo}} (32\text{gm}) \kappa_{\text{O}_2} = n_{\text{mo}} (2\text{gm}) \kappa_{\text{H}_2} = n_{\text{mo}} (18\text{gm}) \kappa_{\text{H}_2\text{O}} =$$

$$n_{\text{mo}} (28\text{gm}) \kappa_{\text{CO}} = n_{\text{mo}} (44\text{gm}) \kappa_{\text{CO}_2} = n_{\text{mo}} R , \quad (1.2)$$

where  $n_{\text{mo}}$  is called the **mole number** or number of moles of the gas in question. What is the significance of this mole number?

The conjecture was made by Gay-Lussac and supported by Avogadro that *at any fixed pressure and temperature, a given volume of any gas contained the same number of molecules*. If so, the mass values above enable one to determine the relative masses of the molecules of various gasses.

Remembering the mass balance for forming water vapor and invoking some further chemistry that determines both ordinary oxygen and hydrogen gas to be composed of the **diatomic** molecules,  $\text{O}_2$  and  $\text{H}_2$ , respectively, it follows that *the oxygen molecule has the mass of 32 hydrogen atoms*. We see (**Fig. 3**) that the masses indicated in (1.2), of all three gases, contain the same number of molecules.



**Fig. 3:** The balance of atoms, molecules and masses in the formation of water vapor from hydrogen and oxygen gas.

Since  $n_{\text{mo}}$  (2gm) of  $\text{H}_2$  and  $n_{\text{mo}}$  (32gm) of  $\text{O}_2$  and  $n_{\text{mo}}$  (18gm) of  $\text{H}_2\text{O}$  all contain the same number of molecules and they all have the same value of  $PV/T$ , that value seems to depend *only* on the number of molecules! Comparison with many other gasses, such as  $\text{CO}$  and  $\text{CO}_2$ , corroborates this idea. Consequently we can write,

$$P V / T = N k = n_{\text{mo}} N_0 k, \quad (1.4)$$

Where  $N$  is the number of molecules,  $N_0$ , the number of molecules in one mole and  $k$ , like  $R$ , is a constant that doesn't depend on which gas is being considered (Boltzmann's gas constant). So a *mole of a chemical is, by definition, a mass in grams of that chemical which is numerically equal to the mass of one molecule of the chemical in units of the hydrogen atom mass*. One mole of any chemical contains the same number of molecules, namely,

$$N_0 = 2\text{gm} / m(\text{H}_2) = 18\text{gm} / m(\text{H}_2\text{O}) = 32\text{gm} / m(\text{O}_2) = \\ 28\text{gm} / m(\text{CO}) = 44\text{gm} / m(\text{CO}_2) = 1\text{gm} / m(\text{H}). \quad (1.5)$$

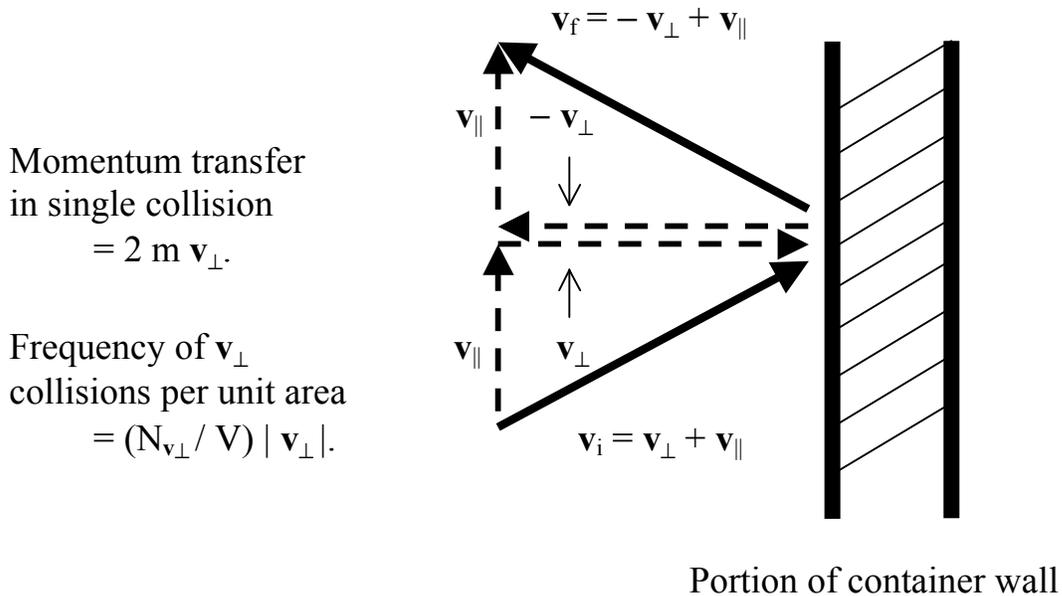
This  $N_0$ , called **Avogadro's number**, has been determined and is roughly, 6 hundred billion trillion!, i.e.,  $N_0 \simeq 6.0 \times 10^{23}$ .

More precisely,  $N_0 = 6.02252 \times 10^{23}$ , but *we* do not need that kind of precision! In other words, in every 18gm of water (just a little more than a cubic inch in volume), or ice or steam, there are about 6 hundred billion trillion  $\text{H}_2\text{O}$  molecules. The same for every 2gm of molecular hydrogen or 32gm of molecular oxygen or 28gm of carbon monoxide or 44gm of carbon dioxide, etc.

Now when one analyses the pressure generated by collisions of the gas molecules with the vessel walls (**Fig. 4**) it turns out that one finds,

$$P = (1/3) n m \langle v^2 \rangle, \quad (1.6)$$

where  $n$  is the number density (number of molecules per unit volume),  $m$  is the mass of a single molecule and  $\langle v^2 \rangle$  is the average squared speed of all the molecules (see **Appendix** for the derivation).



**Fig. 4:** Pressure generation by molecular collisions with container wall.

Since  $n = N/V$ , it follows that

$$PV = (1/3)N m \langle v^2 \rangle = N[(1/3)m \langle v^2 \rangle]. \quad (1.7)$$

Comparing this with the gas law,  $PV = N k T$ , we see that,

$$(1/3)m \langle v^2 \rangle = k T, \quad (1.8a)$$

or

$$(1/2)m \langle v^2 \rangle = (3/2)k T. \quad (1.8b)$$

But the left side of (1.8b) is just the average kinetic energy,  $\langle K \rangle$ , of the gas molecules, i.e., *the absolute temperature is proportional to the average kinetic energy of the gas molecules.*

$$\langle K \rangle = (3/2)k T. \quad (1.8c)$$

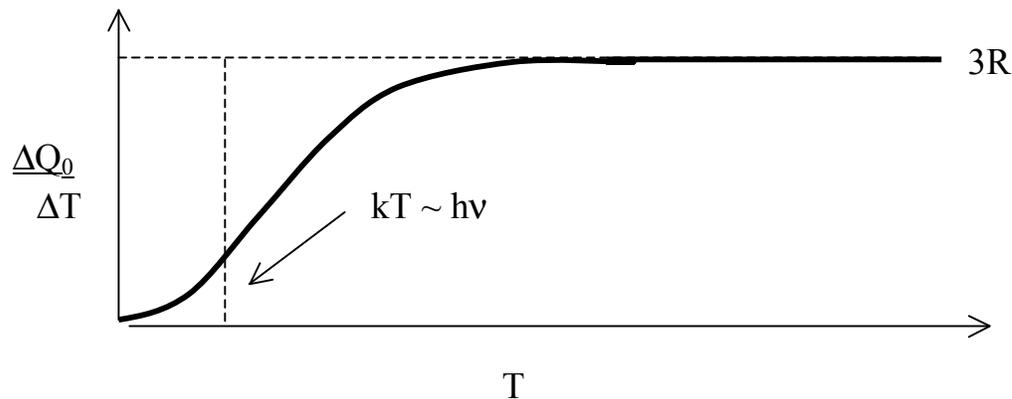
This last relationship appears to hold (with some qualifications) in liquids and solids as well, even though the molecules are subject to forces there.

This result suggests that internal energy is, at least in part, just the kinetic energy of molecules that is uncoordinated among the molecules, i.e.,

involves motion in random directions and with widely varying speeds. For gasses this is pretty much the whole story except that if the temperatures are high enough the molecules will start to individually rotate, as a result of ‘glancing’ collisions and that **rotational kinetic energy** will also be part of the internal energy. In fact, once the temperature is high enough to make the rotational motion common, the average rotational kinetic energy per molecule is again proportional to  $kT$ .

For solids the individual molecules are usually not free to travel far or to rotate but they do vibrate back and forth like harmonic oscillators (**Energy I & II**) around their natural locations within the solid and again, if the temperatures aren’t too low (**Fig. 5**), both the average kinetic and potential energy per molecule are given by  $(3/2)kT$ . Thus the total internal energy per molecule is  $3kT$  and the heat capacity per mole is

$$C_0 = \Delta Q_0 / \Delta T = 3N_0k = 3R \simeq 25 \text{ j / } ^\circ\text{K} = 25 \text{ ws / } ^\circ\text{K}. \quad (1.9)$$



**Fig. 5:** Low temperature deviation of molar heat capacity of solids from classical (Dulong-Petit) value of  $3R \sim 25 \text{ j / K}^0$ .

The details of why temperatures can’t be too low if we are to obtain the simple proportionality of rotational and vibrational energies to  $T$  have to do with quantum mechanics (Notice the  $kT \sim hv$  line in **Fig. 5**. That  $h$  is Planck’s constant and  $\nu$  is the frequency of the molecular oscillations) and were not understood until quantum physics was being developed in the early 1900’s.

## 2: Chemical energies

### a. atoms and molecules

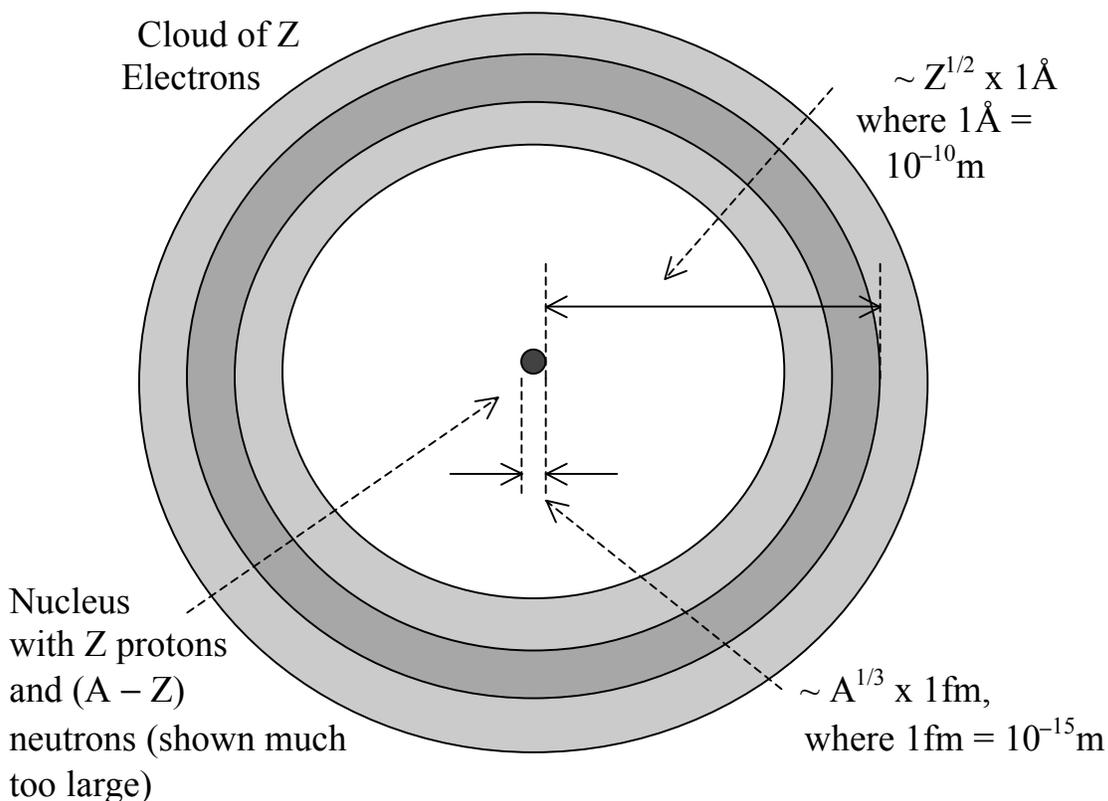
Pure chemical substances are composed of very large numbers of essentially one kind of molecule. When a chemical reaction occurs it usually involves two or more distinct molecules coming together and rearranging their constituent atoms to form two or more new, distinct molecules which, then, move apart. Some reactions generate, or liberate heat and are called **exothermic reactions**. Others require or absorb heat and are called **endothermic reactions**. Which is which and how much heat is involved is determined by examining the energy involved in dissociating molecules into their constituent atoms and forming molecules from their constituent atoms.

But what kind of energy is involved at the atomic and molecular level? The energy due to the motion of the atoms is kinetic, of course, but what of the energies due to the forces that hold atoms together in molecules. What kind of energies and forces are they?

*They are almost all electric forces and electric potential energies, just like the kind we discussed in our first class!* To be sure, a lot of the details concerning how these electric forces produce the atomic and molecular *structures* that they do depends on the laws of **quantum mechanics** which, in many respects, are very strange by comparison with classical, macroscopic mechanics. Nevertheless, as far as the forces and energies, themselves, are concerned; they are mostly electric in nature with additional important electromagnetic contributions in some instances.

The atoms of any given chemical element (**Fig. 6**) are characterized by an integral **atomic number**,  $Z$ .  $Z$  measures (in units of the electric charge,  $e$ , of a proton) the total positive charge ( $q = Ze$ ) of the tiny **nucleus** of the atom which contains almost all the mass of the atom. The nucleus is composed of  $Z$  **protons** ( $q_p = e$ ) and  $A - Z$  uncharged **neutrons** ( $q_n = 0$ ), where  $A$  is called (unfortunately) the **atomic mass** of the atom. The protons and neutrons are held together by much stronger non-electric, **nuclear forces**.

Surrounding the nucleus of a 'normal' (neutral) atom is a cloud of  $Z$  electrons ( $q_e = -e$ ).



**Fig. 6:** Cloud of Z electrons surrounding (99.9999999 % of the volume) a tiny central nucleus (greatly exaggerated) with Z protons and (A - Z) neutrons (99.95 % of the mass).

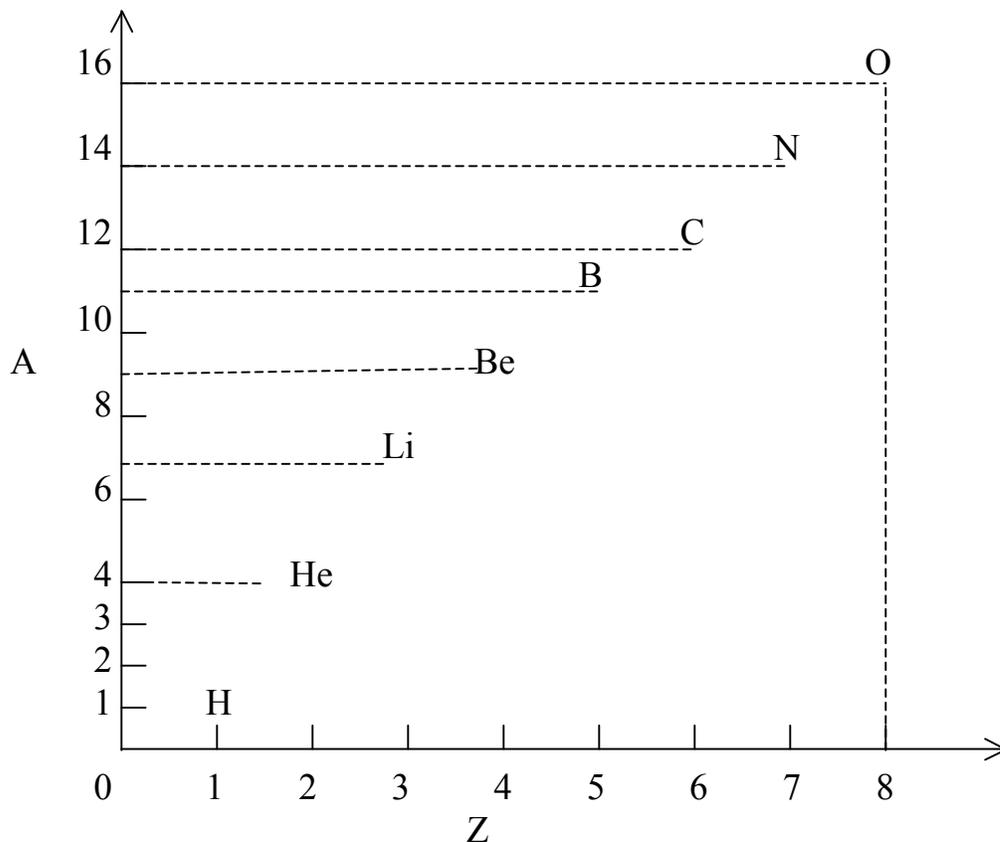
But there are many circumstances in which atoms have one or two more electrons than Z or one or two fewer electrons than Z. In those cases the atoms have a net negative or positive charge, respectively, and are called **ions** or **ionized** atoms. *In chemical reactions only the electrons in atoms change their configurations and distributions.* The nuclei do not change internally and are treated as inert massive point entities. The nuclei of atoms undergo changes only in what are called **nuclear reactions**.

Since protons and neutrons are very nearly of the same mass (the neutron is slightly more massive than the proton) and both are about 1800 times more massive than electrons, the mass of an atom is very close to just A times the mass of a hydrogen atom,

$$m(Z, A) = A m(1, 1) = A m(\text{H}) . \quad (2.1)$$

Through a very long period of examining chemical reactions with ever increasing minuteness and precision, the  $Z$  and  $A$  values for the atoms of all the different chemical elements were determined.

**Fig. 7** lists the values and chemical symbols for the least massive atoms. We notice the tendency for  $Z$  to stay close to  $(1/2)A$ . The reason is that the neutrons help to hold the nucleus tightly together against the electrostatic repulsion of the positively charged protons. As  $Z$  gets larger and larger the number of neutrons required for this purpose slowly exceeds  $Z$  and  $A$  slowly exceeds  $2Z$ . The most common form of uranium has  $Z = 92$  and  $A = 238$ ! The less stable form with  $A = 235$  is used in reactors and the bomb.



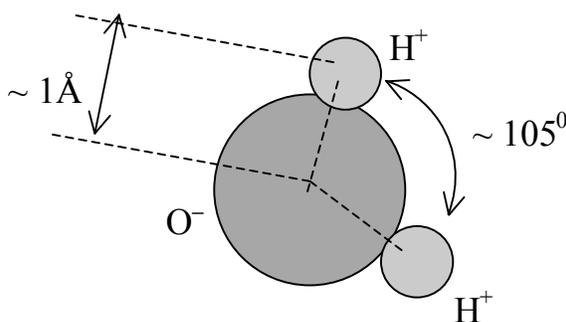
**Fig. 7:** The symbols, atomic numbers ( $Z$ ) and atomic masses ( $A$ ) for the least massive atoms.

Some other common atoms that are important in daily life are (using the notation: Symbol( $Z$ ,  $A$ ))

F(9, 19), Ne(10, 20), Na(11, 23), Mg(12, 24), Al(13, 27),  
 Si(14, 28), P(15, 31), S(16, 32), Cl(17, 35), Ar(18, 40),  
 K(19, 39), Ca(20, 40), - - - , Mn(25, 55), Fe(26, 56), Co(27, 59),  
 Ni(28, 59), Cu(29, 64), Zn(30, 65), - - - , Ag(47, 108), - - - ,  
 Au(79, 197), - - - , Pb(82, 207), - - -

The symbol and name of a chemical element is rigidly attached to a single  $Z$  value because the number of electrons in the neutral atom determines the chemical properties of a substance. The  $A$  values can vary a little bit, the different  $A$  values for a given  $Z$  value corresponding to what are called the **isotopes** of the chemical element. I have given the  $A$  values for the most commonly occurring isotopes.

I've said that the forces involved in chemical reactions and atomic and molecular structure are predominately electrical in nature. Let's consider the water molecule in that regard (**Fig. 8**). Each hydrogen atom normally has one electron negative cloud around its nucleus while the oxygen atom has an 8 electron cloud around its nucleus. When a hydrogen and an oxygen atom get as close as they are in a water molecule the laws of quantum mechanics favor a distortion of the



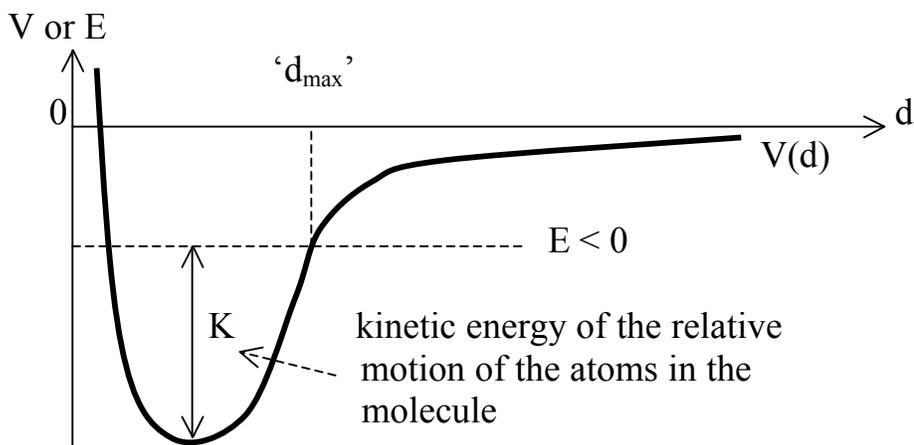
**Fig. 8:** Electrostatic geometry of the water molecule

electron clouds so that the hydrogen electron and one of the oxygen electrons tend to concentrate a bit more around the oxygen than around the

hydrogen nucleus. This partial stripping of the hydrogen of its electron cloud makes the hydrogen end of the chemical bond somewhat positive and the oxygen end somewhat negative. The attraction between the atoms is now a combined effect of the sharing of an electron pair, a strongly quantum mechanical effect, and the electrostatic attraction between the somewhat positive H and the somewhat negative O. If only one hydrogen is bonded the stripping effect is so strong that the hydrogen quickly picks up an additional free electron and we have the negative **hydroxyl ion**,  $\text{OH}^-$ . With two bonded hydrogens we get the neutral water molecule,  $\text{H}_2\text{O}$  with the distortion of the electron clouds such as to leave the hydrogen and oxygen ends of the molecule forming what is called an **electric dipole moment**. This strong dipole moment makes water very effective as an almost universal solvent. A third hydrogen can attach itself to the oxygen but now the charge cloud distortion actually undermines the ability of the molecule to hold onto enough electrons to neutralize the charge and we obtain the positive **hydronium ion**,  $\text{H}_3\text{O}^+$ .

### b. reaction energies

Both the electron sharing and the separation of oppositely charged regions leads to attraction between the atoms. This attraction is associated with negative potential energy (**Fig. 9**), as our discussion of electrical attraction indicated in **Energy I**, and that negative potential energy more than compensates the positive kinetic energy of the nuclei and electrons.

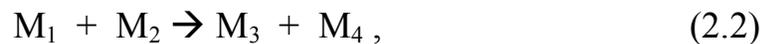


**Fig. 9:** Schematic effective potential energy binding atoms in a molecule. The energy required to pull the atoms apart is  $|E|$ .

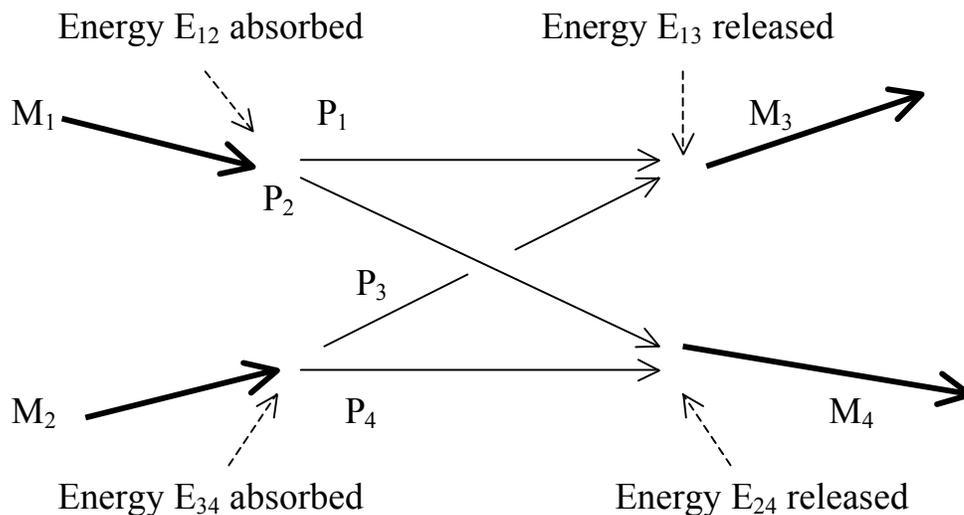
Consequently, if one is going to pull the water molecule apart into its hydrogen and oxygen constituents, one must deposit enough energy to overcome the net negative energy holding the molecule together.

Suppose two molecules come together and react to form two different molecules that then separate. The overall reaction usually requires that each molecule be pulled apart to some degree and the parts then reassembled into the final molecules. What is it that determines the circumstances under which the reaction will occur?

Consider a reaction (**Fig. 10**) (the  $M_n$  are molecules, the  $P_m$  are parts of the molecules, i.e., atoms or smaller molecules),



where  $M_1 = P_1P_2$ ,  $M_2 = P_3P_4$ ,  $M_3 = P_1P_3$  and  $M_4 = P_2P_4$ .



**Fig. 10:** Absorption and release of binding energies in the schematic reaction,  $M_1 + M_2 \rightarrow M_3 + M_4$ .

Let  $E_{12}$  be the energy required to pull  $M_1$  apart into  $P_1$  and  $P_2$ , called the **binding energy**. Let  $E_{34}$  be the energy required to pull  $M_2$  apart into  $P_3$  and  $P_4$ . Let  $E_{13}$  be the energy required to pull  $M_3$  apart into  $P_1$  and  $P_3$  and, finally,

let  $E_{24}$  be the energy required to pull  $M_4$  apart into  $P_2$  and  $P_4$ . When the parts come back together again to form the original molecules, the binding energies are released.

This means that to pull  $M_1$  and  $M_2$  apart into the P's requires an energy of  $E_{12} + E_{34}$ , while to pull  $M_3$  and  $M_4$  apart into the P's requires an energy of  $E_{13} + E_{24}$ .

So if  $M_1$  and  $M_2$  are pulled apart and the parts are reassembled into  $M_3$  and  $M_4$ , the energy  $E_{12} + E_{34}$  is first required (absorbed) and then the energy,  $E_{13} + E_{24}$ , is released. If the latter energy exceeds the former the reaction will spontaneously occur if the initial collisions between  $M_1$  and  $M_2$  molecules are strong enough to pull them apart (high enough temperature) and the reaction will release a net energy of,

$$E_{\text{release}} = (E_{13} + E_{24}) - (E_{12} + E_{34}) . \quad (2.3a)$$

On the other hand, if the former energy is greater than the latter, then, even with  $M_1M_2$  collisions strong enough to pull them apart, the reaction will not occur unless additional energy,

$$E_{\text{required}} = (E_{12} + E_{34}) - (E_{13} + E_{24}) , \quad (2.3b)$$

is available to drive it. In the first case we have an **exothermic reaction** since it releases energy. In the second case an **endothermic reaction** since it absorbs energy.

But how does one determine these separate energies for pulling apart and assembling single types of molecules? Today there are many methods, but an old and still standard method is to examine appropriate sets of common reactions. For example, consider the reactions,



where all the reactions occur at standard atmospheric pressure and at 25°C and everything except the carbon, C, is a gas. The pure C is in the form of graphite. The energies per mole on the right take into account the work that is done by the expansion under pressure of the generated gasses, CO<sub>2</sub> and CO, and the work done on the contraction under pressure of the disappearing gasses, O<sub>2</sub> and CO.

From the listed reaction energies we can determine how much more energy is required to remove one O atom from a CO<sub>2</sub> molecule than is required to remove the remaining O atom from the CO molecule.

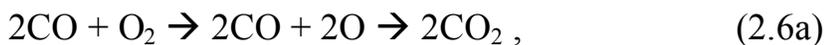
The argument goes like this: The second reaction must proceed in the steps,



So first we break up 1/2 mole, say, of O<sub>2</sub> (requiring energy (1/2)E<sub>O<sub>2</sub></sub>) and then we form 1 mole of CO (liberating energy E<sub>CO</sub>). Referring back to the table we have,

$$E_{CO} - (1/2)E_{O_2} = 111 \text{ kJ/mo} . \quad (2.5b)$$

Next we note that the third reaction must proceed in the steps,



requiring breakup of 1/2 mole of O<sub>2</sub> (energy (1/2)E<sub>O<sub>2</sub></sub>) followed by formation of 1mole of CO<sub>2</sub> from CO and O (liberating energy E<sub>CO<sub>2</sub>/CO</sub>). From the table,

$$E_{CO_2/CO} - (1/2)E_{O_2} = 283 \text{ kJ/mo} . \quad (2.6b)$$

Now notice that if we subtract (2.5b) from (2.6b) we get,

$$E_{CO_2/CO} - E_{CO} = (283 - 111) \text{ kJ/mo} = 172 \text{ kJ/mo}, \quad (2.7)$$

telling us that 172 kJ/mo more energy is released when the second oxygen atom is combined with a CO molecule than when the first oxygen atom combined with a carbon atom. So adding that second O atom tightens up the CO<sub>2</sub> molecule, noticeably, over the CO molecule!

Finally, while the first reaction, (2.4a), doesn't have to proceed in steps, it *can* do so and often will and the energy released will be the same (This is **Hess' law**; if not nature could get energy for nothing by running the reaction in steps in one direction and not in steps in the other). But the stepwise version is,



Involving the  $\text{O}_2$  breakup (energy  $E_{\text{O}_2}$ ) followed by the CO formation (energy  $E_{\text{CO}}$ ) followed by the  $\text{CO}_2$  formation (energy  $E_{\text{CO}_2/\text{CO}}$ ). Consequently,

$$E_{\text{CO}_2/\text{CO}} + E_{\text{CO}} - E_{\text{O}_2} = (283 + 111) \text{ kJ/mo} = 394 \text{ kJ/mo}. \quad (2.8b)$$

Therefore the 394 kJ/mo value for the first reaction is *determined* by the 111 and 283 values for the other reactions by the simple addition of equations (2.5b) and (2.6b). By Hess's law (really just a chemical instance of the law of energy conservation) the 394 value couldn't have been anything else!

By studying the  $\text{O}_2$  molecule in detail we can determine that breaking up a mole of  $\text{O}_2$  into two moles of atomic oxygen requires 249 kJ, i.e.,



Substituting into (2.5b) and (2.6b) we find

$$E_{\text{CO}} = 236 \text{ kJ/mo} \quad \text{and} \quad E_{\text{CO}_2/\text{CO}} = 408 \text{ kJ/mo} \quad (2.10)$$

### c. hydrocarbons

So much for the burning of carbon. What about the problem of the age: the burning of **hydrocarbons**!?

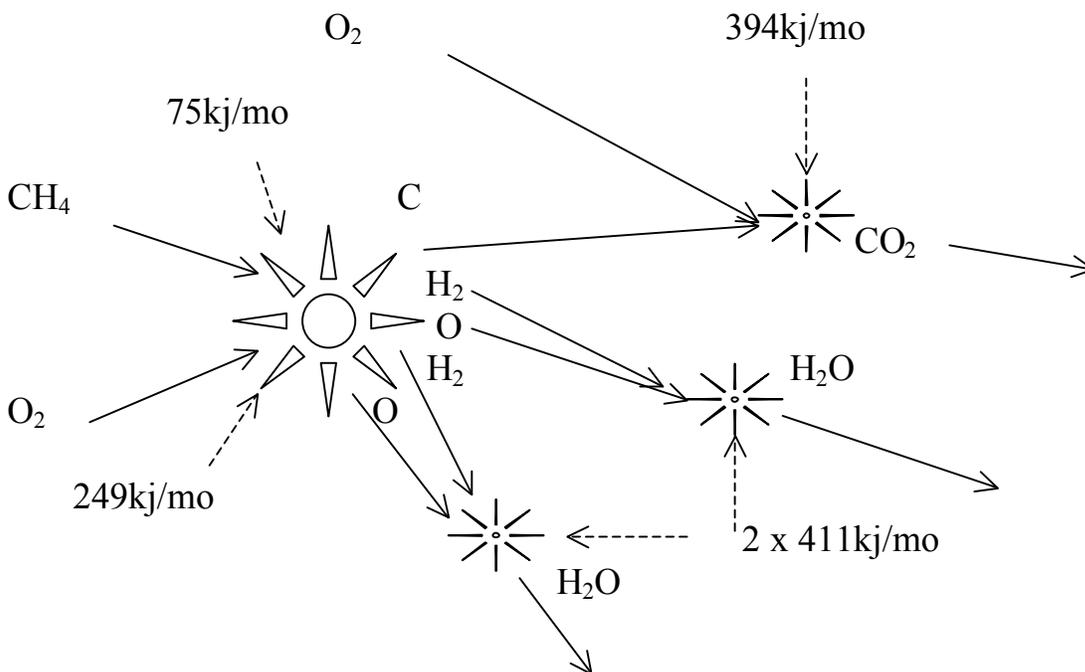
Burning oil or gas or kerosene or gasoline or methane, etc., are all exothermic reactions which release energy as heat. The purpose of the match or spark plug discharge or pilot light that initiates the reaction is to get the oxygen and hydrocarbon molecules colliding violently enough in a tiny region to pull them apart. Once begun, the energy released by the recombination with oxygen is sufficient to keep the collisions strong and the reaction ongoing.

Regardless of the number of molecules participating in a reaction the energy considerations remain the same. Whether the reaction releases or absorbs energy depends on the comparison of the energies required to break the initial molecules apart and the energies released when the final molecules form.

A simple example of hydrocarbon burning is the burning of methane (**Fig. 11**),



a three molecule to three molecule reaction. We can regard this as a two step process in which the first collision between the methane and one oxygen molecule breaks the  $\text{O}_2$  into two O atoms and the  $\text{CH}_4$  into three parts, C and



$$\text{Net energy release:} = (411 + 411 + 394) \text{ kJ/mol} - (249 + 75) \text{ kJ/mol}$$

$$= (1216 - 324) \text{ kJ/mol} = 892 \text{ kJ/mol} \quad (2.11\text{b})$$

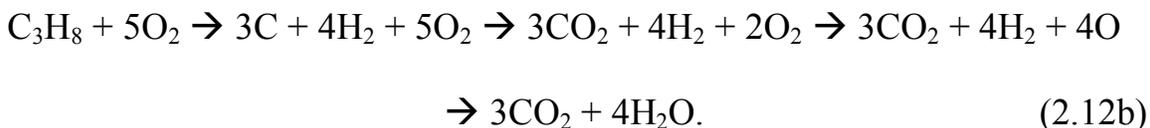
**Fig. 11:** A molecular scenario for the burning of methane with the calculation of the molar energy release.

two H<sub>2</sub> molecules. Next the C collides with another O<sub>2</sub> to form CO<sub>2</sub> while the two H<sub>2</sub>s join with the Os to form water, H<sub>2</sub>O. The net energy release is 892 kJ per mole of methane.

A similar analysis can be done for the burning of propane. The propane molecule is a bit more complex, C<sub>3</sub>H<sub>8</sub>, and the reaction analysis of the six molecules to seven molecules burning reaction,



Using Hess's law, employs the steps,



The first step pulls the propane molecule apart into constituent carbon atoms as graphite and hydrogen molecules. The energy for doing that at standard temperature and pressure is 108 kJ/mo(C<sub>3</sub>H<sub>8</sub>).

The second step involves combining three O<sub>2</sub> molecules onto three C atoms and we previously found, (2.4a), that process to release 394 kJ/mo(CO<sub>2</sub>). For each mole of propane we start with we will produce 3 moles of CO<sub>2</sub>. So the energy released in this second step will be 3 x 394 kJ = 1182 kJ/mo(C<sub>3</sub>H<sub>8</sub>).

The third step breaks up the two remaining O<sub>2</sub> molecules into 4 O atoms which, by (2.9), will require 2 x 249 kJ = 498 kJ/mo(C<sub>3</sub>H<sub>8</sub>).

The last step combines 4 hydrogen molecules with 4 oxygen atoms to form 4 water molecules and, from **Fig. 11**, this will release 4 x 411 kJ = 1644 kJ/mo(C<sub>3</sub>H<sub>8</sub>).

So, the net energy released from the burning of one mole of propane is

$$\begin{aligned} -108 \text{ kJ} + 1182 \text{ kJ} - 498 \text{ kJ} + 1644 \text{ kJ} &= (2826 - 606) \text{ kJ} \\ &= 2220 \text{ kJ/mo(C}_3\text{H}_8\text{)}. \end{aligned} \quad (2.12c)$$

Comparing propane with methane we find that one mole of propane gives more than twice the energy release of one mole of methane, but it also

produces three times as much of the greenhouse gas,  $\text{CO}_2$ , as the methane does. On the other hand, gram for gram, the energy release and  $\text{CO}_2$  production for methane is:

$$(892 \text{ kJ} / \text{mo CH}_4) / (16 \text{ gm} / \text{mo CH}_4) \simeq 56 \text{ kJ} / \text{gm}$$

and

$$(1 \text{ mo CO}_2 / \text{mo CH}_4) / (16 \text{ gm} / \text{mo CH}_4) \simeq 0.06 \text{ mo CO}_2 / \text{gm}.$$

While for propane we have:

$$(2220 \text{ kJ} / \text{mo C}_3\text{H}_8) / (44 \text{ gm} / \text{mo C}_3\text{H}_8) \simeq 50 \text{ kJ/gm}$$

and

$$(3 \text{ mo CO}_2 / \text{mo C}_3\text{H}_8) / (44 \text{ gm} / \text{mo C}_3\text{H}_8) \simeq 0.07 \text{ mo CO}_2 / \text{gm}.$$

Gram for gram methane and propane are not so different while mole for mole they are! Which is the more important comparison?!

### **Appendix: Gas pressure and average squared velocity**

For a given small portion of the wall of a gas containing vessel, the contained molecules can be divided up (in our imagination) into groups with different ranges of values for the component of their velocity that is perpendicular to the given portion of the wall,  $v_{\perp}$ . We put  $v_{\perp} > 0$  if a molecule is heading towards the wall and  $v_{\perp} < 0$  if heading away from the wall. For purposes of statistical analysis the groups must be chosen so that  $v_{\perp}$  is nearly constant within a group while, at the same time, the number of molecules in a group,  $N(v_{\perp})$ , is large enough to be uniformly distributed throughout the container. These are competing demands.

Now consider a layer of gas, next to the wall portion of interest, that is thin enough so that any molecule within it that has  $v_{\perp} = v_{\perp,1} > 0$  will collide with the wall before colliding with another molecule. Let the thickness of the layer be  $d_1$ . Each such molecule will transfer  $2 m v_{\perp,1}$  in momentum to the wall portion as a consequence of bouncing off the wall (**Fig. 4**). If the area of the wall portion is  $A$  then the volume of the layer over  $A$  will be  $Ad_1$ . The number of molecules within this volume that have  $v_{\perp} = v_{\perp,1}$  will be,

$$N_1 = (N(v_{\perp,1})/V) Ad_1, \quad (\text{A.1})$$

and everyone of these molecules will collide with the wall portion within the time interval,

$$t_1 = d_1 / v_{\perp, 1}. \quad (\text{A.2})$$

So the rate with which these molecules transfer momentum to the wall portion is,

$$\begin{aligned} (N_1/t_1) 2 m v_{\perp, 1} &= \{[N(v_{\perp, 1})Ad_1/V]/d_1\} 2 m v_{\perp, 1}^2 \\ &= 2 m v_{\perp, 1}^2 [N(v_{\perp, 1})/V] A. \end{aligned} \quad (\text{A.3})$$

A rate of momentum transfer has the physical character of a force and this is the force exerted by these collisions on the wall portion. The pressure from this force results from dividing by the area,  $A$ ,

$$P_1 = (2 m / V) v_{\perp, 1}^2 N(v_{\perp, 1}). \quad (\text{A.4})$$

Next we sum all the quantities of this kind for all positive values of  $v_{\perp}$  to get the total pressure on the wall portion. Assuming this includes half of all the molecules (the other half have negative  $v_{\perp}$ ) we can write,

$$\sum_{v_{\perp} > 0} v_{\perp}^2 N(v_{\perp}) = \langle v_{\perp}^2 \rangle N / 2, \quad (\text{A.5})$$

where  $\langle v_{\perp}^2 \rangle$  is the average value of  $v_{\perp}^2$  over all the molecules (the average for positive  $v_{\perp}$  being the same as for negative  $v_{\perp}$ ). The total pressure is then,

$$P = (2 m / V) \langle v_{\perp}^2 \rangle N / 2 = (N / V) m \langle v_{\perp}^2 \rangle = n m \langle v_{\perp}^2 \rangle, \quad (\text{A.6})$$

where,  $n = N / V$ , the molecular number density.

Now if the gas as a whole is not moving, the molecules display no preference for any particular direction of motion over any other. Consequently the average, over the molecules, of the square of a component of the velocities in any one direction will not vary with the direction. But, by Pythagoras' theorem, the square of a velocity is the sum of the squares of the components of the velocity in any three mutually perpendicular directions,

$$v^2 = v_x^2 + v_y^2 + v_z^2. \quad (\text{A.7})$$

The average of the square of the molecular velocities must, then, be the sum of the averages of the squares of components of the velocities in any three mutually perpendicular directions and these latter averages must all be the same. Therefore,

$$\langle v^2 \rangle = 3 \langle v_{\perp}^2 \rangle, \quad (\text{A.8})$$

or

$$P = (1/3) n m \langle v^2 \rangle, \quad (\text{A.9})$$

as was to be shown.