3 Properties and State of a Substance

3.1 In An Ideal World

3.1.1 Outline

In this unit we will review molar mass, moles and molecules. We will introduce the empirical gas laws and introduce the equation of state for an ideal gas. We will then consider what is an ideal gas and finally demonstrate how to manipulate the equation, to relate one state to another.

3.1.2 Moles

Let's start with a mole. A mole is a unit of measurement typically employed in chemistry to represent amounts of a substance. By definition a mole of any substance is that number of mass units equal to the molar mass of the substance and we can choose any mass unit we would like to use.

We work with consistent SI units and the mass unit in SI units is the kg. So we can define a kmol using the kg mass unit. For example, the molecule Oxygen has a molar mass of 32, so therefore one kmol of oxygen will have a mass of 32 kg. Notice how the letter k has been placed in front of the mole to indicate a kmol.

We could use grams instead, so for example the hydrogen molecule has a molar mass of two so therefore 1 gmol of hydrogen will have a mass of two grams. Note, in chemistry texts it is quite common to work in units of grams and gmols, often dropping the prefix ‘g’ and referring to mols.

We could use the imperial pound so, for example, one lb mol of carbon dioxide, which has a molar mass of 44, will have an absolute mass of 44 imperial pounds.

You can use any mass unit even for example, a tonne !

At any time we can calculate the number of moles simply by taking the mass of the substance and dividing by the molar mass of the substance. You will see examples of this later

3.1.3 Molar mass

Here are some examples of the molar mass of a few common substances, we will work with these later. In this course it is not necessary for you to remember the molar mass of substances, but they can be helpful to give you an idea of the scale and magnitude of numerical calculations.

Notice how air has also been given a molar mass. Of course air is a mixture of gases, but it is convenient to assume that we can define a molar mass for air to use in our calculations. We will define air to consist of, on a volume basis, 21% oxygen, 78% nitrogen, and 1% argon. With a corresponding molar mass of 28.97 kg/kmol.

3.1.4 Molar Mass, Moles and Molecules

Why not explore and learn more about moles and molar mass.

http://ed.ted.com/lessons/1207-1-a-bennet-brianh264

3.1.5 Introducing the empirical gas laws

There are three important empirical gas laws, referred to as Avogadro's Law, Boyle's Law and Charles' Law. The ABC's of the gas laws. You have probably seen these already, but it is useful to review their statements.

3.1.6 Avodadro's Law

In 1811 Avogadro hypothesised that for a given mass of an ideal gas, the volume and the amount in moles, were directly proportional to each other, for a fixed temperature and pressure. That is the volume is linearly proportional to the number of moles.

We can state Avogadro's Law as

"equal volumes of gas under the same temperature and pressure contain the same number of molecules"

So for example, for any gas at a temperature of 273K and a pressure of 101325Pa, that is a standard atmosphere, then, making sure we work in consistent units, one kmol of a gas, of any gas, will have a volume of 22.4m^3. We will repeat this calculation later and you'll see how you can determine the volume of gas using the equation of state for an ideal gas.

3.1.7 Amedeo Avogadro (1776–1856)

Why not explore and learn more about Amedeo Avogadro.

http://www.chemheritage.org/discover/online-resources/chemistry-in-history/themes/the-path-to-the-periodic-table/avogadro.aspx

3.1.8 Robert Boyle

Robert Boyle was a leading intellectual figure of the 17th century and one of the founders of modern chemistry. He observed that the pressure of a gas was inversely proportional to its volume and you can see this in the animation, that as we change the pressure so we compress or expand the gas and its volume changes accordingly.

We can state Boyle's Law as

"the absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies, provided that temperature and the mass of gas remain unchanged within a system"

3.1.9 Robert Boyle (1627-1691)

Why not explore and learn more about Robert Boyle.

http://www.bbc.co.uk/history/historic_figures/boyle_robert.shtml

http://jap.physiology.org/content/98/1/31.full#F2

Robert Boyle's landmark book of 1660 with the first experiments on rarified air, John B. West, Journal of Applied Physiology January 1, 2005 vol. 98 no. 1 31-39

3.1.10 Charles' law

Jack Charles and Joseph Gay-Lussac were French scientists around the turn of the 17th Century and independently they observed that at low pressures the volume of a gas is proportional to its temperature. You can see this illustrated in the animation below, that as we change the volume of the gas its temperature will change, provided we keep the pressure constant.

We can state Charles' Law as

“the volume of a given mass of an ideal gas is directly proportional to its temperature on the absolute temperature scale provided pressure and the mass of gas remain unchanged”

3.1.11 Jacques Charles and Joseph Gay-Lussac

Why not explore and find out more about Jacques Charles and Joseph Gay-Lussac.

http://www.century-of-flight.net/Aviation%20history/to%20reality/jaques%20charles.htm

http://www.chemheritage.org/discover/online-resources/chemistry-in-history/themes/early-chemistry-and-gases/gay-lussac.aspx

3.1.12 The Empirical Gas Laws

From the empirical gas laws, we have Boyle's Law which states that pressure is inversely proportional to volume; Charles's Law which states that volume is proportional to temperature and Avogadro's Law which states that the volume is proportional to the amount of substance present.

We can combine these three expressions and derive the following expression, which states that the product of pressure and volume, divided by temperature, is equal to the number of moles present multiplied by some constant of proportionality.

3.1.13 The Equation of State on a Molar Basis

The constant of proportionality has been determined for various gases, both experimentally and analytically. This is now referred to as the *universal gas constant* which takes a standard value of 8314 J/(kmol K)

This equation is referred to as the Equation of State for an Ideal Gas and we note that in the SI sytem of units, the units of the universal gas constant are in J/(kmol K).

We will to this equation as the equation of state for an ideal gas on a molar basis.

Another important point, you must always remember that the units of temperature must be on an absolute temperature scale, which in SI units, are units of kelvin.

3.1.14 Equation of State on a Mass Basis

Now working in moles is often unfamiliar, it would be more convenient to work in units of mass. We state again the equation of state on a molar basis. You can see how we can determine the number of moles if the mass and the molar mass are known.

Substituting the number of moles into the equation of state on a molar basis and manipulating the algebra, allows us to derive a new equation of state for an ideal gas on a mass basis.

3.1.15 Equation of State on a Mass Basis

Notice now that the constant of proportionality, the gas constant on a mass basis, which is referred to here as Rgas, is not actually a constant ! Rgas is defined to be equal to the universal gas constant divided by the molar mass of the particular gas being considered, so therefore the gas constant on a mass basis is only a constant for a given gas and the gas must be defined.

We can see in the example below that for nitrogen, with a molar mass of 28 kg/kmol, then we can determine the gas constant for nitrogen on a mass basis, which is actually equal to 296.9 J/(kg K)

Again note and always remember that temperature must be in units of kelvin.

3.1.16 Mass and Density

We can manipulate the equations a little bit more. Stating again the equation of state on a mass basis, let us rearrange the equation in terms of mass. You can see in this equation how we can determine the mass of a gas present in a closed system, provided pressure, volume, temperature and the gas constant for that particular gas are known.

The expression can be further rearranged to allow us to calculate density. Remember density is mass per unit volume. You can see now how we can determine the density of any gas if pressure, temperature and the gas constant for that particular gas are known.

Something important, the symbol that is used by convention for density is the Greek symbol rho, but look how similar the symbol is to the lower case symbol, p, for pressure, you must never confuse or mix up rho for density and P for pressure. I'll try to point this out on future occasions.

3.1.17 Ideal Gas

The term “ideal gas” has been used without any definition.

An Ideal Gas is by definition, an idealisation. However many real gases do approximate the behaviour of an ideal gas. The concept of an Ideal Gas is based upon the following assumptions :

i. Gases are made up of molecules which are in constant random motion in straight lines.
ii. The molecules behave as rigid spheres and pressure is due to collisions between the molecules and the walls of the container.
iii. All collisions are perfectly elastic with no loss of kinetic energy during the collision.
iv. The temperature of the gas is proportional to the average kinetic energy of the molecules.
v. There are no intermolecular forces between the gas molecules.
vi. The volume occupied by the molecules themselves is negligible relative to the volume of the container.

Now the question is, when is a gas an ideal gas ? For simplicity, let us make a definition,

“an ideal gas is any gas that obeys the ideal gas equation of state”

So therefore from the definition an ideal gas, if we look at the ratio of the terms, and let's call the ratio the compressibility factor, then for an ideal gas, that ratio will always be equal to unity. For any gas that does not follow this behaviour, we will refer to as a real gas. That is for a real gas, the compressibility factor will not be equal to one.

3.1.18 Real Gases

The question is how far away do real gases depart from the behaviour of an ideal gas. Here we can see the compressibility factor, PV divided by RT plotted as a function of pressure, in atmospheres, for a selection of gases.

At first sight it looks like these gases significantly depart from that the behaviour of an ideal gas, but notice, look at the pressure scale on the x-axis, on the far right hand side the pressure is 1000 atmospheres and we notice that as the pressure reduces all of the gases tend to the behaviour of an ideal gas.

Remember the assumption that for an ideal gas, molecules have perfectly elastic collisions, that is there are no intermolecular forces. This must be incorrect for all gases, because at low temperatures all gases condense to form a liquid phase.

Also, at high pressures, and thus high densities, the intermolecular distances will become quite short, and attractive forces between molecules must therefore become significant. Equally, the actual volume taken up by the molecules will become significant. Hence we can expect significant departures at high pressures and when a gas condenses.

For realistic engineering calculations we are often only interested in relatively low pressures and at relatively low pressures these gases can be assumed to approximate that of an ideal gas.

3.1.19 Air as an Ideal Gas

The behaviour of air is particularly important. Here we can see the compressibility factor, PV divided by RT for air, plotted as a function of pressure, in units of bar. Remember 1 bar is equal to 100,000 Pa, approximately the same as one standard atmosphere.

You can see again how at low pressures the compressibility factor tends toward one. In the table in the upper right we can see the effect of temperature and pressure on the value of the compressibility factor. You can readily see that over a temperature range from 250 to 500K and from 1 to 10 bar pressure, the compressibility factor is very nearly equal to 1, and so therefore we can assume that over this range, air may be assumed to approximate an ideal gas.

At other conditions when a gas cannot be assumed to be an ideal gas then we must use another equation of state for a real gas, but in this course we will only work with the equation of state for an ideal gas.

3.1.20 Manipulating the Equation of State

We can manipulate the equation of state a little bit more, here again we have written the equation of state for an ideal gas, subtly rearranged as PV divided T equal to nR. In this case the equation is presented in molar units. Notice how on the right hand side only a term involving constant factors remains, for a fixed amount of gas. Therefore the ratio, PV divided by T, is equal to some constant for a given amount of gas.

Let's say now we have two different arbitrary conditions, and identify them as state 1 and state 2. Writing down the equations, we can say that at state 1 the ratio PV over T, is equal to a constant. Similarly at state 2, PV over T is equal to the same constant value.

This is a re-statement of the equation of state. Equating the two terms on the left and the right hand side of the expression yields a relationship between pressure, volume and temperature at these two arbitrary states. This expression will be used many times in the future when we change state from one condition to another condition.

3.1.21 Simplified State Changes

We can make a general statement now, based on the equation of state for an ideal gas, which states that at any arbitrary condition, the ratio PV divided by T is equal to a constant , which is therefore equal to any other arbitrary condition.

This now allows us to define three simpler forms of the relationship.

Firstly, if the temperature is constant, then temperature cancels out from the expression and we are left with the relationship P1 V1 is equal to P2 V2. Secondly, if the pressure is constant then pressure cancels out and we are left with V1/T1 is equal to V2/T2. And finally, if the volume is constant then P1/T1 is equal to P2/T2. Remember that the states 1 and 2 are arbitrary.

We will refer to these three particular conditions as; isothermal, if the temperature remains constant; isobaric, if the pressure remains constant and isochoric if the volume remains constant.