3.2 What a state we are in !

3.2.1 Outline

In this unit we will consider the different physical forms that a substance may take and how they may be represented in terms of properties.

We will start by defining the phase of a substance. This will allow us to define a homogenous mixture which will then help us to introduce the concept of pure and simple substances. Followed by the introduction of thermodynamic properties and the state of a substance allowing us to explore the idea that the state depends upon thermodynamic properties. Finally we will introduce some intensive and extensive properties and how we may convert between the two.

3.2.2 Phase

Let's start with a reminder about what we understand about the phase of a material.

A phase is defined as having a distinct molecular arrangement that is homogenous throughout and separated from other phases by easily identifiable boundary surfaces. The two distinct phases of solid and liquid water represent a good example of this. We will be concerned with the three common phases, solid, liquid and gas.

A gas is a sample of matter that conforms to the shape of the container in which it is held and one which acquires a uniform density inside the container even in the presence of gravity and regardless of the amount of substance in the container. The atoms or molecules of matter in the gaseous state move freely amongst each other. A gas may be compressed or expanded to change the mass per unit volume.

A liquid is a sample of matter that also conforms to the shape of the container in which it is held, but unlike a gas, a liquid does not readily disperse to fill every space of the container but takes on a defined surface in the presence of gravity. Some liquids resist compression while others can be compressed. Both gases and liquids may flow and are often referred to as fluids. A fluid will continuously deform when a force is applied.

A solid is a sample of matter that retains its shape and density when not confined. It is characterised by structural rigidity and resistance to changes of shape or volume when a force is applied. Unlike a liquid, a solid object does not flow to take on the shape of its container nor does it expand to fill the entire volume available to it like a gas.

3.2.3 Homogenous mixture

Now it is quite possible that we may have different combinations of substances present, we need to make some simplifying definitions.

We will start by defining a homogenous mixture, which in thermodynamics, is defined as a mixture where all substances are in the same phase and it should not be possible to separate the different substances. So for example, air, which is a mixture of various gases, and wine, a mixture of liquid water and liquid alcohol are both excellent examples.

But oil and liquid water would not be a good example, where we can see that the two distinct substances can be clearly identified with a distinct interface.

3.2.4 Pure Substances

Once we have the concept of mixtures then we have to consider how many different substances might be present and in what form. We will now introduce the definition of a pure substance.

In thermodynamics, a pure substance may be defined in one of three ways, firstly as a single substance, which has the same chemical composition throughout, for example, oxygen or nitrogen or water. Secondly as a single phase mixture, of any number of substances, provided they are all in the same phase, that is, a homogenous mixture. So gaseous air and the mixture of liquid water and alcohol are both excellent examples.

Finally a pure substance can be defined when there is a mixture of two or more phases, provided the chemical composition is the same. So for example, ice and liquid water can be considered a pure substance but not the combination of gaseous nitrogen and liquid oxygen because they are different substances.

3.2.5 Simple Substance

In the simplest case, a single substance that is only present in a single phase is referred to as a simple substance. Liquid water is one such example.

3.2.6 Properties and state of a substance

Now that we have introduced a homogenous mixture and the concept of substances and pure substances we need to consider how and when they can exist.

We introduce a new term, *state,* and make the following definition - the phase of a material or a substance may exist at various states, where an individual state is defined by some combination of macroscopic properties, by which we imply thermodynamic properties such as temperature and pressure.

We will introduce this idea by considering for example, ice, which we know exists at certain temperatures, but that it will melt if the temperature increases above zero Celsius. So we have this idea that a material can only exist in a certain form at specific values of a property, such as temperature.

Thermodynamic properties can be defined as some property for which a definite value exists for some state. For example the range of temperatures when ice can form.

Similarly, a property is a quantity that depends upon the state of the system. So, in the case of solid water, such as ice, we know that as the solid water melts and turns into liquid water and even changes phase again into steam, so the property temperature changes. We can then say that temperature is a thermodynamic property.

Another very important feature of a thermodynamic property is that they are independent of the way the values change from one state to another - so it doesn't matter for example how we heat up the ice and how rapidly the temperature changes.

You will see later how we may say that the value of a property, for example, temperature, is always independent of the path taken to change state.

3.2.7 Water Phase Diagram

Here is a good example which illustrates the phase diagram for water. At first sight it looks complex, but we can see some key points. To start with, the X axis represents variation in temperature and the Y axis represents variation in pressure, which happen to be in units of Celsius and MPa. We can see also that the phase diagram illustrates the three different phases of water, solid, liquid and vapour.

We can see the blue region, which is solid water, we would refer to that as ice. We can see the green region which is identified as liquid and we can see the brown region which is identified as vapour.

We may consider this phase diagram to be rather like a geographic map, where in this case, temperature and pressure are the coordinates which allow us to locate position on the phase diagram or the map.

3.2.8 How many properties required ?

One good question is how many properties do we require to define the state of the system ? Previously we could see that there were two properties, pressure and temperature. Does that define whether we have ice or liquid water ? Do we need more properties to strictly identify what we have ? On a map we typically have just two coordinates, for example latitude and longitude.

The number of properties required to define the state of a system is known as the state postulate and can be expressed as "the state of a simple compressible system is completely specified by two independent, intensive properties".

A simple compressible system is one where there are no external force fields such as electrical or magnetic or gravitational fields and for us, a simple compressible system is the most common system that we will encounter in typical engineering situations. If any of these additional forces do exist then it is necessary to include an additional property when defining the state of the system.

3.2.9 Thermodynamic Properties

We have introduced the terms *independent* and *intensive properties* so now we must define these as well. But what do we mean by a property and particularly a thermodynamic property ?

Here are some examples in this word cloud. You can see there is energy and temperature, pressure, mass and others that are more unusual properties, for example heat capacity and concentration, colour, moles and charge.

3.2.10 Thermodynamic Properties – Extensive

Let us start by defining an extensive property, this is a subset of all possible properties. An extensive property can be defined as "a physical quantity which is the sum of the properties of separate non interacting subsystems that compose the entire system".

That is a complex definition, but what this means is that an extensive property varies with the amount of mass. So in the illustration we can see a block of yellow cheese. What is quite obvious is that if we cut the cheese into two big chunks, labelled X1 and X2, then the total mass of cheese remains unchanged, and is simply the sum of the two chunks X1 and X2.

Other examples include for example length and volume, weight and momentum. If we cut the cheese into two different lengths, and put them back together, we will recover the original length (unless someone eats the cheese in the meantime !).

3.2.11 Thermodynamic Properties - Intensive

On the other hand there are some properties which are clearly independent of the mass, for example the colour of the cheese was not going to change regardless of how many slices we cut it into. In the same way, for a liquid or gas, the pressure is independent of the mass and the temperature is independent of the mass in a closed volume. This is easy to demonstrate for temperature, just consider pouring a kettle of hot water into two cups – the water in the cups will initially have the same temperature as that in the kettle.

Other intensive properties include density and viscosity and for solids include ductility and elasticity, perhaps surprisingly, the melting point and the boiling point and even the colour or the smell are independent of the mass and perhaps might be considered as intensive thermodynamic properties.

Something to note, fortunately we can always convert from an extensive property to an intensive property simply by dividing by the amount of mass.

We often use the word *specific* to identify that now we have an intensive property that is on a per unit mass basis. For example, the name *specific volume* would refer to volume per unit mass and so specific volume is independent of the amount of mass and is an intensive property.

Another good way to remember the two different types of properties, intensive and extensive - *intensive* properties are *independent* of the amount of mass.

3.2.12 Independent Properties

I also introduced the concept of independent properties. Formally, two properties are defined as being independent if one property can be varied while the other is held constant.

So imagine we have some sort of piston cylinder arrangement. We can change the volume of the free space in the cylinder by moving the piston in or out and we can ensure that the temperature remains the same by either heating or cooling the cylinder as we move the piston. In this example, volume and temperature are clearly independent of each other.

Now consider two other possible properties, specific volume and density. Remember that specific volume, which was introduced a little earlier, is volume per unit mass, and we know that density is mass per unit volume. So the answer to this question is NO ! The two terms are not independent because they are just the inverse of each other.

3.2.13 Independent Properties – Phase Change

Let us consider another combination, pressure and temperature. Yes we can use these for single phase systems, but it is much more complicated for multiphase systems involving phase change. The complication is that when we change the phase of a material it is not possible to fix the pressure and vary the temperature independently. We will explore this in a later section.

So for the time being we will state that we can use temperature and pressure as independent properties when we have a single phase system and we can use those to define the state of that system. But should we ever have any change of phase, for example boiling or solidification than we can no longer use temperature and pressure as the two properties to define the state of a system.

3.2.14 Equilibrium

Finally we must define another term, *equilibrium,* for which you probably already have a good understanding.

We can define mechanical equilibrium, that is when an object is static or it is in a state of unchanging motion. By that we mean that the net force acting on the object is equal to zero.

We can define thermal equilibrium when there is no energy transferred into or out of the system.

We can define phase equilibrium when there is no mass transfer between for example solid phase and the liquid phase.

We can define chemical equilibrium when the substances are not changing their chemical composition over time. That is it is constant.

Finally we can define thermodynamic equilibrium. That is we require that the thermodynamic properties do not change with time.

3.2.15 Example of a state diagram : Pressure - Volume

Here is an example of a state diagram. A state diagram illustrates the state of a pure substance, in a simple compressible system, as two independent properties are changed.

In this example we have two properties, pressure and volume. So remember that this must be for a single phase system. We will assume it is for a gas and you can see that the state of the system is changing, as indicated by the pink and blue lines. The state changes continuously, going from points 1 to 2 to 3, and identified by the terms isobaric expansion and isothermal expansion.

We will introduce these two terms later, but you can see how they are referring to changes occurring either at constant pressure (isobaric) or constant temperature (isothermal).

You can see the two lines are indicating how we are changing the state by varying either pressure or volume independently or in combination together.

3.2.16 Example of a state diagram : Enthalpy – Entropy Diagram

Here is another much more complex example using properties that we have not yet introduced, enthalpy and entropy. Also overlaid on this enthalpy-entropy diagram are pressure and temperature.

3.2.17 Example of a state diagram : Mollier Diagram

Here is another pressure enthalpy diagram, commonly referred to as a Mollier Diagram. It is very complex but has traditionally been used in engineering before the advent of computer systems. In this case the diagram shows the variation of two properties, pressure and enthalpy, but also identifies temperature on the red lines and specific volume on the green lines. Such diagrams are very useful when understanding refrigeration and power cycles.

3.2.18 Richard Mollier (1863-1935)

Why not explore and find out more about Richard Mollier, the name now given to all diagrams that involve enthalpy.

http://www.thermopedia.com/content/966/