## 3.5 Freeze dried coffee

### 3.5.1 Outline

In this unit we will continue to investigate the phenomena of phase change. The concept of a solid melting to a liquid and then evaporating to become a gas or vapour is easy to understand, but is it possible to skip a step ? In this unit we will see how that might happen and why it might be useful to us.

We will revisit phase diagrams, and identify the critical point in the triple point.

The terms of vapour and gas very common. We will review the difference between what is implied by the two terms.

We will review the different mechanisms of phase change and introduce a new process, sublimation.

The theatrical effect of "dry ice" has become very common. We will discover what "dry ice" really is and why it apparently gives off a mist like vapour.

Finally we will explore the process of freeze-drying and how this takes advantage of the phenomena of sublimation.

### 3.5.2 Phase diagram for water

Here again we can see the phase diagram for water, plotted as a function of pressure against temperature and illustrating the three different phases that water may take, solid, liquid and vapour.

We have already introduced the saturated liquid-vapour line and the effect of pressure on boiling point.

The transition from liquid like behaviour, to gas like behaviour, is not necessarily abrupt and it may be difficult to say exactly where the liquid region ends and where the gas region starts. This is especially the case as we approach the critical point, to the far right on this diagram.

The single phase liquid region, also known as the sub-cooled or compressed liquid region, is to the left of the two phase region. The region is sometimes referred to as the compressed liquid region, because if the pressure is reduced the liquid will evaporate to become a vapour. The region is sometimes considered to exist until the critical temperature is reached. The region is also sometimes referred to as a sub-cooled liquid because its temperature is lower than the saturation temperature at the same pressure, that is lower than the boiling point.

The single phase vapour region, is to the right of the two phase region. The region is also known as the superheated vapour region, because it’s temperature is greater than the saturation temperature at the same pressure, that is higher than the boiling point. This region is often, perhaps arbitrarily, considered to end at the isobar corresponding to the critical pressure.

Notice on the phase diagram that, whilst there are distinct transitions from one phase to another, there is one single point, referred to as the Triple Point, where a substance exists in three phases in equilibrium. The corresponding conditions are referred to as the Triple Point pressure and temperature.

At the Triple Point pressure and temperature, all three phases are in equilibrium. For water, the critical point is at a temperature of 0.01°C and pressure of 0.6117 kPa.

Notice the critical point to the far right the saturation line. Let's just revisit this again.

### 3.5.3 Critical point

In a previous module we discovered the existence of the so-called critical point when investigating the variation of saturation temperature with pressure. The critical point is defined as the point at which the saturated liquid and saturated vapour states are identical. Beyond the critical point it is no longer possible to distinguish between liquid and vapour.

At the critical point pressure and temperature, the saturated liquid and saturated vapour states are identical. This coincides with the top of the two phase dome. The specific volume at the critical point is referred to as the critical volume.

The table in the upper right illustrates some typical critical point data. Notice that the critical point for water is at a temperature of 374.14°C and a pressure of 22 MPa. Whilst for example, that of carbon dioxide is only at a temperature of 31°C and a pressure of 7.39 MPa.

### 3.5.4 What is the difference between vapour and gas

The two terms, vapour and gas, are in everyday use. But it is often confusing to understand what is actually being referred to and what is the difference between the two terms. Does it matter which term we use ?

A simple rule of thumb suggests that if a substance is a liquid at ambient conditions, then we typically refer to it as a vapour, when in the gaseous state. Water vapour is the most common example. Similarly, if a substance is in the gaseous state at ambient conditions, then we would commonly refer to the substance as a gas.

Perhaps formally we could define a vapour as a substance in the gas phase at a temperature lower than its critical point. By referring to the phase diagram. We can see that a vapour could be condensed to a liquid or even to a solid, by increasing the pressure without reducing the temperature.

Whereas a gas might be considered to exist at a temperature above the critical temperature. A substance at a pressure greater than the critical pressure and greater than the critical temperature is often referred to as a supercritical fluid.

So for example, the critical temperature for water is 647 K, or 374°C, that is why we commonly refer to water vapour rather than water gas, since other than at extreme temperatures we are always below the critical temperature for water.

Similarly the critical temperature for oxygen is -118.35°C, that is why at typical ambient conditions, we refer to oxygen as a gas, rather than a vapour, since in this case we are well above the critical temperature.

For most substances the gas–liquid–solid Triple Point is also the minimum temperature at which the liquid can exist. For water, however, this is not true because the melting point of ordinary ice decreases as a function of pressure, as shown by the dotted green line in the phase diagram.

### 3.5.5 Three-dimensional phase diagram

You have seen that we can represent the different phases of a substance on a phase diagram in terms of pressure and temperature. You have also seen that during the phase change between liquid and vapour the two thermodynamic properties, pressure and temperature are no longer independent and we must employ another, thermodynamic property, for example, volume.

It is possible to illustrate the phase diagram in terms of these three thermodynamic properties as an isometric three-dimensional surface.

On the left you can see a three-dimensional phase diagram, in terms of pressure, volume and temperature, for a substance that contracts on freezing. Notice the step decrease in volume when the substance freezes.

In contrast, on the right you can see a phase diagram for a substance that expands on freezing, such as water. Although it is less clear in this isometric view, notice the step increase in volume when the substance freezes.

As an aside, for a substance that expands on freezing, such as water, then by definition, it's volume will increase for a given mass. Therefore the density will decrease. It is this phenomena that is responsible for ice floating on water. A further surprising physical characteristic of liquid water is that it's maximum density occurs at a temperature of 4°C. This means that on a frozen lake the solid ice is on the surface yet the water below is above freezing point. This characteristic is essential for marine life to be able to exist through the winter periods and is another fascinating example for why animal life on Earth depends upon the unique properties of water.

### 3.5.6 Two-dimensional phase diagram

Generally it is more convenient to work with two-dimensional phase diagrams, such as the pressure, volume and temperature volume diagrams.

Here, on the left, you can see a pressure, volume diagram for a substance that contracts on freezing, and on the right for a substance that expands on freezing. On the pressure, volume diagram, the triple point is seen to exist as a line, the Triple Line, where liquid and vapour exist as a saturated mixture.

### 3.5.7 Phase transition

Just a reminder about phase transition from solid to liquid to vapour. Remember that for transition to occur from solid to liquid to vapour, energy is required to be absorbed, referred to as the latent heat of fusion or vaporisation. Similarly for transition from vapour to liquid to solid, energy is released to the environment, which by conservation of energy, is equivalent to the corresponding latent heats of fusion or vaporisation.

You can also see two other possible phase transition routes, the direct transition from a solid to a vapour, referred to as sublimation, and from vapour to solid as deposition.

Let's explore these in more detail.

### 3.5.8 Sublimation

Referring to the phase diagram on the right, sublimation refers to the phase transition directly from solid to vapour. You can see that this occurs at temperatures and pressures below that of the Triple

Point. This implies that at low pressures, below the triple point value, solids will evaporate without melting.

This phenomena is responsible for the theatrical effects referred to as dry ice.

### 3.5.9 What is dry ice?

This might look like a witches cauldron in a glass beaker ! The effect has been created by placing a piece of solid carbon dioxide in a beaker of water. The carbon dioxide is not melting, but is undergoing the phase transition of sublimation, that is directly changing from solid to vapour. As a consequence, the still relatively cold carbon dioxide vapour escapes and the moist air above the liquid water condenses, forming water droplets. The mist we can see is actually minuscule water droplets. This is the phenomena originally responsible for theatrical fog before the advent of smoke generators.

### 3.5.10 Dry ice

Why not explore more and find out about dry ice.

http://www.youtube.com/watch?v=6JzQ08AGuhI

### 3.5.11 Phase diagram for carbon dioxide

The phenomena of dry ice can be explained by looking at the phase diagram for carbon dioxide, as illustrated here. Note that pressure, in units of kPa, is on a logarithmic scale and that temperature in units of Kelvin is on a linear scale.

The triple point and the critical point have been highlighted, together with atmospheric pressure, which takes an approximate value of 100 kPa.

The triple point for carbon dioxide is at a temperature of 216 K and a pressure of 517 kPa. Now you can see why, when a piece of solid carbon dioxide is taken from cold storage and placed at room temperature and atmospheric pressure, sublimation takes place. Atmospheric pressure is below the Triple Point for carbon dioxide and so as the solid carbon dioxide absorbs heat from the liquid water, phase transition occurs as sublimation.

This is not a phenomena just restricted to carbon dioxide, all substances will undergo sublimation at the corresponding pressure and temperature below the Triple Point.

### 3.5.12 Freeze-drying

The phenomena of sublimation can surprisingly be taken advantage of to remove the water content from foodstuffs and dry other products. The process is commonly referred to as freeze-drying.

The freeze drying procedure can be illustrated by considering the phase diagram for water, shown on the left. In this case the Triple Point for water has been highlighted, which occurs at a temperature of 273.16 K and a pressure of 0.61 kPa.

During the freeze-drying process, fresh or cooked foods are first flash frozen, when the food tastes its best. This occurs in a pressure vessel but at atmospheric pressure. The pressure is then reduced below the Triple Point pressure, to vacuum levels. Moisture is then removed in the vacuum chamber, where a low-level heat is applied to transform the solid ice to vapour, through sublimation, without returning it to a liquid form.

Since the product remains frozen during the process, the product cell structures do not change, retaining the freshness, vitamins, nutrients, colours, and aromas of the fresh foods while offering the shelf stable convenience of long-term storage.

The freeze-drying process allows for quick rehydration of the product, making freeze-dried foods ideal for food storage. Because the liquid moisture has been removed, freeze-dried products are light, they typically weigh up to 90% less than the products original weight, hence their popularity with campers and backpackers !

### 3.5.13 Freeze-dried coffee

Why not explore and find out more about the process of freeze-drying?

http://www.youtube.com/watch?v=cuPdf3bFqZE

### 3.5.14 What happens to water in space?

This is another question for you to explore. What do you think happens to water in space? Does the water freeze to first, turning to solid, or boil immediately, turning to vapour? The first video answers this question.

http://www.youtube.com/watch?v=UG7nsZkVZc0

What about on top of a mountain? The second video is an entertaining answer to this question.

http://www.youtube.com/watch?v=wJ3CKgZEitw

Why not explore and find out more about what happens to water at extreme temperatures and pressures.