Pure Substances

1 Introduction to Pure Substances

A **pure substance** is a substance that has a fixed chemical composition. This can be a mixture of elements, as long as the mixture is homogeneous.

Pure substances can come in various phases. In a **solid**, the molecules are arranged in a three-dimensional pattern (the lattice) that repeats through the material. In a **liquid** the molecules can move and rotate freely, but are still quite close together. Finally, in a **gas**, the molecules are far apart from each other.

When dealing with pure substances, often the quantity $u + Pv$ is encountered. This quantity has therefore been given its own name. The **enthalpy** h is thus defined as

$$h = u + Pv. \tag{1.1}$$

2 Vaporizing a Liquid

Let's suppose we want to vaporize a liquid to its gas form. Initially the liquid is not about to vaporize. We say it is a **compressed liquid** or a **subcooled liquid**. We then add heat. After a while, the liquid will be about to vaporize. We now call it a **saturated liquid**. When part of the liquid has vaporized, and part has not, we have a **saturated liquid-vapor mixture**. Finally, when all the liquid has vaporized and we only have vapor left, we have a **saturated vapor**. This vapor it still about to condense. If we heat it further, then it won't be about to condense any more. We are then dealing with a **superheated vapor**. The heat which is absorbed to make the phase change is called the **latent heat**.

At a given pressure, the temperature at which pure substances change phase is called the **saturation temperature** T_{sat}. Identically, for a given temperature, the pressure at which the phase changes is called **saturation pressure** P_{sat}. A plot of these two is called a **liquid-vapor saturation curve**. Such a plot is shown in figure 1.
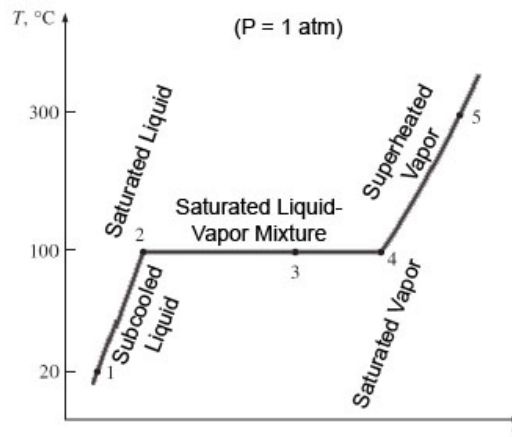

Figure 1: The liquid vapor saturation curve for water.

3 Mixture Quality

When the liquid is saturated, it has a certain specific volume v_f. Identically, the saturated vapor has a specific volume v_g. The change in specific volume v_{fg} is then defined as $v_{fg} = v_g - v_f$. Identically the **enthalpy of vaporization** (or **latent heat of vaporizaton**) is defined as $h_{fg} = h_g - h_f$. In the critical point, which will be discussed soon, both v_{fg} and h_{fg} are zero.

During vaporization there will be a mixture of liquid and vapor. The **quality** x of this mixture (having a value between 0 and 1) is defined as

$$x = \frac{m_{vapor}}{m_{total}}. \tag{3.1}$$

The **average specific volume** of the mixture can be found using

$$v_{avg} = \frac{m_{liquid}v_f + m_{vapor}v_g}{m_{total}}. \tag{3.2}$$

Now the quality of the mixture can also be calculated using

$$x = \frac{v_{avg} - v_f}{v_{fg}}. \tag{3.3}$$

Usually v_f and v_{fg} are known for a substance. Only the average specific volume then needs to be measured to find the quality of the mixture. And once the quality is known, the average internal energy u_{avg} and the average enthalpy h_{avg} can be found using

$$u_{avg} = u_f + xu_{fg}, \qquad \text{and} \qquad h_{avg} = h_f + xh_{fg}. \tag{3.4}$$

4 $T - v$ Diagrams

The variations of properties during phase-change processes are best studied and understood with the help of **property diagrams**. There are $T-v$, $P-v$ and $P-T$ diagrams. First let's consider $T-v$ diagrams.

The $T-v$ diagram for water is shown in figure 2. When vaporizing water at low pressures, there still is a region in which a saturated liquid-vapor is present. This region is called the **saturated liquid-vapor region**. To the left of this region is a **subcooled liquid region** and to the right is a **superheated vapor region**.
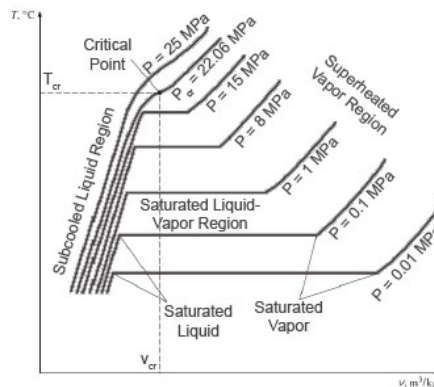

Figure 2: Diagram plotting the temperature versus the specific volume.

There are many saturated liquid points now. The line connecting these points is called the **saturated liquid line**. This line separates the subcooled liquid region from the saturated liquid-vapor region. The

line connecting the saturated vapor points is called the **saturated vapor line**. The point where these two lines meet is the **critical point**. Corresponding to this point are the **critical temperature** T_{cr}, the **critical pressure** P_{cr} and the **critical specific volume** v_{cr}.

The $P - v$ diagram is very similar to the $T - v$ diagram. But although the v increases with increasing T, the specific volume v decreases for increasing P. So while the lines in figure 2 go upward, in a $P - v$ diagram they go downward.

5 $P - T$ **Diagrams**

Given the pressure and temperature of a substance, its phase can be derived. This is done using $P - T$ diagrams. Such a diagram is shown in figure 3.
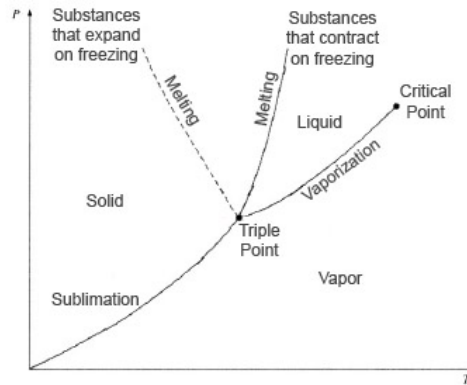

Figure 3: Diagram showing the phase of a pure substance, given its pressure and temperature.

So we see that at low pressures it is possible for a solid to change to a gas without becoming liquid. Also, at high pressures (higher than the critical pressure), a liquid can turn to a gas without any clear transition. But maybe the most interesting point in figure 3 is the **triple point**. This is the point where all three phases can coexist in equilibrium.

Now we have discussed $T - v$, $P - v$ and $P - T$ diagrams. However, there are also $P - v - T$ diagrams. These are three-dimensional diagrams, consisting of a so-called $P - v - T$ **surface**. Using this surface, it is usually possible to determine one of the three properties, once the other two are known.

6 **Property Equations**

It's nice to have graphs showing the relation between properties. But sometimes it's more convenient to have an equation that does the same thing. Any equation that relates the pressure, temperature and specific volume of a substance is called an **equation of state**. The problem is that there is no equation of state that always works.

The most well-known equation of state is the **ideal-gas equation of state** (or **ideal-gas relation**), stating that

$$Pv = RT. \tag{6.1}$$

Here R is the **gas constant**, which differs per gas. For high specific volume gases this equation is rather accurate. However, as the state of the gas becomes closer to the saturated vapor line, this equation loses its accuracy.

This equation can be made more accurate, using the **compressibility factor** Z, defined as

$$Z = \frac{Pv}{RT}. \tag{6.2}$$

Let's also define the **reduced pressure** P_R and the **reduced temperature** T_R as

$$P_R = \frac{P}{P_{cr}} \qquad \text{and} \qquad T_R = \frac{T}{T_{cr}}. \tag{6.3}$$

Now, for every type of gas, the factor Z only (approximately) depends on the reduced pressure and temperature. This principle is called the **principle of corresponding states**.

There are many (more complicated) equations of state. A few examples are the **Van der Waals Equations of State**, the **Beattie-Bridgeman Equation of State**, the **Benedict-Webb-Rubin Equation of State** and the **Virial Equation of State**. All the above equations of state have certain coefficients which need to be determined by experiments. Generally we can say that the more coefficients an equation has, the more accurate it is.