Thermodynamic Properties

Before we discuss the meaning of the word property, it is important to review an underlying concept. A *pure substance* is one whose chemical composition is homogeneous and invariant. Consider, for example, a tank containing liquid water. If the water is heated until it boils, it will contain a two-phase mixture of liquid H_2O and H_2O vapor. No matter whether we sample the liquid part or the vapor part, the chemical composition is still H_2O. It's a pure substance! On the other hand, if we start with a homogeneous mixture of oxygen and methane and allow it to burn, its chemical composition will change to H_2O, CO, CO_2 and other products of combustion. It's not a pure substance since its chemical composition was not invariant. For the following discussion of thermodynamic properties, all substances are assumed to be pure.

A *property* of a substance is any measurable characteristic. Linear dimension, mass, electrical resistance, viscosity, thermal conductivity, temperature, pressure and color are examples of the properties of a substance. Not all properties are relevant to the thermodynamic analysis of systems important to engineers, however. For example, odor (yes, it can be measured) would probably not be useful to us in the solutions of engineering problems, but might be important when considering the suitability of a substance for certain applications.

The thermodynamic properties of a pure substance are divided into two groups: *intensive properties* and *extensive properties*. Intensive properties are independent of mass and therefore don't depend on the size of the sample being examined to determine the property. For example, the density (mass per unit volume) of a sample of water is the same whether we're looking at a cubic foot of water or a cup of water. It's an intensive property. The same would be true of viscosity (the resistance to flow), electrical resistance, thermal conductivity, specific volume, pressure or temperature. These properties are all independent of sample size and are intensive.

Extensive properties, on the other hand, depend directly on the mass of the sample being examined. Examples of extensive properties are volume, mass itself and energy. Some common extensive properties are frequently converted to intensive properties by dividing by the system mass. For example, specific volume is total volume divided by total mass. Upper-case symbols are usually used to denote extensive properties (e.g., V is used for total volume or U for total internal energy) and lower-case symbols are used to denote intensive properties (e.g., v for specific volume and u for specific internal energy).

A *simple-compressible substance* is one for which surface forces (e.g. surface tension) or body forces (gravity, magnetic, etc.) are unimportant. This term is usually used in conjunction with the term "pure" (recall the earlier definition) to describe the substances familiar to engineers: air, water, etc. Everything discussed here will pertain to pure, simple-compressible substances.

Two properties are *independent* if there can exist multiple values of one property (for example, pressure) while the second property (for example, temperature) remains constant and the phase description is unchanged. An example of this would be superheated water vapor, where, for a particular temperature, an infinite number of pressure values can exist with the phase description still being that of a superheated vapor.

Two properties are *dependent* if, for a particular phase description, there can exist one and only one value of one property for each value of the other property. An example of this is two-phase (saturated) H_2O, where for each temperature there can exist one and only one pressure if the substance is to remain saturated, that is, if it is to not move into the superheated or compressed region of the phase map. In this saturated region, a second independent property, frequently specific volume, is used to fix the state of the system.

If two independent, intensive properties are known for a pure, simple-compressible substance, its thermodynamic state is completely known. This is termed "fixing" the state of the substance and implies that all other thermodynamic properties can now be determined.

The word *phase* refers to a portion of a substance in which the physical structure as well as chemical composition is homogeneous. A homogeneous physical structure would be completely solid, liquid or gaseous, but not a combination of any two or three of these attributes. When multiple phases are present, there are definite bounding surfaces separating the phases. Different substances can be combined in a homogeneous mixture, for example liquid water and liquid alcohol, to form a single liquid phase. Similarly, gaseous mixtures can form a single gaseous phase (for example oxygen and nitrogen). Immiscible substances such as liquid water and oil would combine to form two liquid phases. In reality, there are at least twelve phases of ice, but these are of little interest in typical engineering problems.

Temperature

Everyone intuitively knows that the word temperature refers to the "hotness" or "coldness" of an object or substance. A formal definition, however, of something so fundamental is difficult to give. Instead, engineers define equality of temperature in terms of thermal equilibrium. Consider two aluminum castings, one hot and one cold. If we measure the thermodynamic properties (density, electrical resistance, etc.) of each casting, we find that the properties are different for each casting, since properties are, in general, a function of temperature. If we now bring the castings into thermal contact and isolate them from their surroundings, we note that the measurable properties begin to change. Heat flows from the hot body to the cold body causing the thermal energy to equalize. Eventually, no further property changes are observed in either casting, and they are said to be in thermal equilibrium with one another. Equality of temperature has been achieved. We can deduce that this physical property that tells us when two objects are in thermal equilibrium is the property we call temperature.

Common sense tells us that when two objects are in thermal equilibrium with a third object, they are in thermal equilibrium with each other. This is the *zeroth law of thermodynamics*, and is the basis for all temperature measurement. When we wish to know if two objects are at the same temperature, we bring each into thermal contact with a third object – a thermometer – and compare the readings on an arbitrary scale.

These *temperature scales* are defined by assigning an arbitrary number to some easily-reproducible reference point. This point is by international agreement the triple point of water, where the vapor, solid and liquid phases exist together in thermodynamic equilibrium. A temperature of 273.16 Kelvin or 491.7 Rankine is assigned to this point. These are known as *absolute temperatures* and are related by the equation

$$T \text{ (°R)} = 1.8 \ T \text{ (°K)}.$$

The *Celsius scale* is defined so that the temperature of the ice point (what we usually think of as the freezing point of water) is 0.00 C or 273.15 K and the steam point is 100.00 C or 373.15 K. The *Fahrenheit scale* assigns a value of 32 F to the ice point and 212 F to the steam point.

Therefore, the various temperature scales can be related by the following equations:

$$T \text{ (°K)} = T \text{ (°C)} + 273.15$$
$$T \text{ (°R)} = T \text{ (°F)} + 459.67$$
$$T \text{ (°F)} = 1.8 \ T \text{ (°C)} + 32$$

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The P-v-T Surface

The figure shows a three-dimensional surface formed by plotting all possible thermodynamic states for water as a function of pressure, specific volume and temperature. It should be noted that water is a substance which expands on freezing. Most substances contract on freezing and the P-v-T surface for these would have a slightly different appearance.
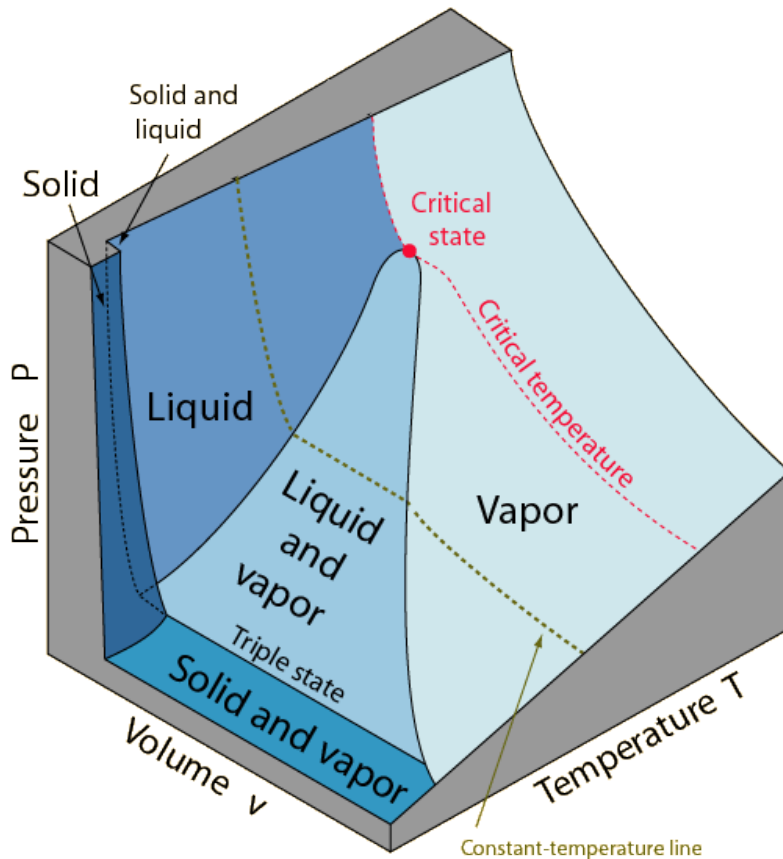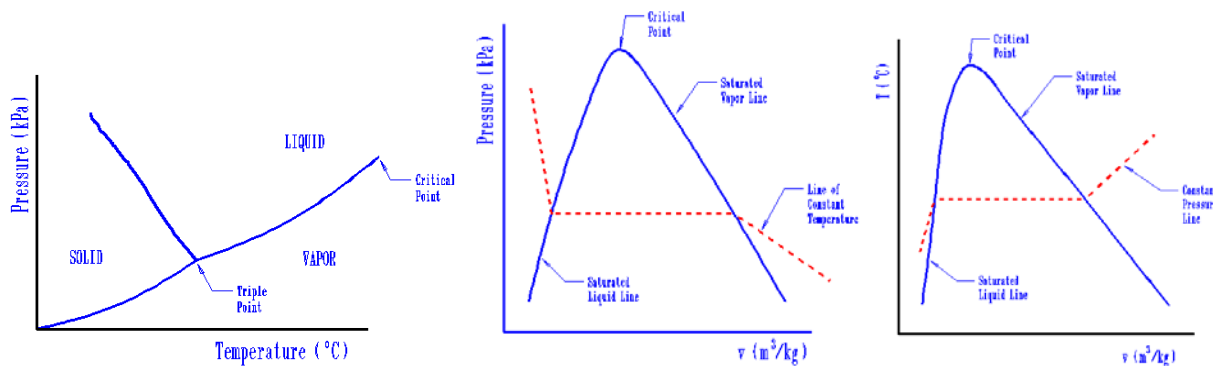
The regions labeled solid, liquid and vapor are the single-phase regions where pressure, specific volume and temperature are all independent. Therefore, any two of the three properties would fix the state.

Separating these single-phase regions are the two-phase (saturated) regions where two phases can exist together in thermodynamic equilibrium: liquid-vapor, solid-liquid, or solid-vapor. Within these two-phase regions, pressure and temperature are not independent; if one changes, the other must change. Therefore, if pressure and temperature for a two-phase mixture are specified, the remaining properties (specific volume, internal energy, etc.) cannot be determined. A second independent property, such as specific volume, is required to fix the state. The three phases can exist together along a line labeled *triple line*. Recall that this is the reference state for our temperature scales.

The *critical point* is also labeled in the figure. At pressures and temperatures above the critical values two-phase mixtures cannot exist.

It is frequently beneficial to view the P-v-T surface perpendicular to any two of the primary axes, thus forming a P-v, T-v or P-T diagram. These views are shown in the figures.

When viewed perpendicular to the pressure and temperature axes, the two-phase regions are shown in edge view as lines separating the single-phase regions (labeled solid, liquid and vapor). The triple line is now shown in end view as a point.

The second figure shows the P-v-T surface viewed perpendicular to the pressure and specific volume axes. Lines of constant temperature (isotherms) are shown. Notice that the isotherms are horizontal in the two-phase regions, indicating that pressure and temperature are not independent there.

The third figure shows the P-v-T surface viewed perpendicular to the temperature and specific volume axes. Lines of constant pressure (isobars) are shown. Notice that the isobars are horizontal in the two-phase region where pressure and temperature have a one-to-one correspondence: for each temperature, there can exist one and only one pressure.

An interesting and instructive thought experiment can be carried out while viewing the temperature-specific volume diagram. Suppose we start with a container of single-phase liquid water (slightly subcooled, as we might get from a regular faucet). We're going to heat the water at constant pressure until it is entirely vaporized into superheated steam. The apparatus for this might be a vertical cylinder fitted with a frictionless piston of fixed weight, thus keeping pressure constant. As we start out along the isobar, we're moving up and to the right (temperature and specific volume are both increasing). As we continue to add heat, however, we reach a point where volume continues to increase, but temperature no longer increases and is constant. Ponder that for a moment: We're heating the water but temperature is constant! This makes sense because we've entered the two-phase region where temperature and pressure are not independent: if one is constant the other is constant. Eventually we see temperature start to increase again and we realize we've left the two-phase region and entered the single-phase superheated steam region. This reinforces our concept of the pressure vs. temperature behavior of water while reminding us of the distinction between heat and temperature.

As mentioned earlier, two independent, intensive properties fix the state of a pure, simple-compressible substance. This means that if two independent, intensive properties are known, all the other properties for that particular thermodynamic state can be determined. For example, if temperature and specific volume are known then values for pressure, internal energy, enthalpy, entropy and all other properties can be found.

For example, water at 100 kPa with a specific volume of 1.0 m^3/kg is found to be a two-phase mixture of liquid and vapor since the specific volume is between the saturated liquid value and the saturated vapor value. If the specific volume had been greater that the saturated vapor value at that pressure, the water would have been in a superheated state, and would be a single-phase vapor. If the specific volume had been less than the saturated liquid value at that pressure, the water would have been in the subcooled (compressed) state,

and would be a single-phase liquid. Once the state has been located on the phase diagram, the desired properties can be found from the steam tables.

Latent and Sensible Heat

The terms *latent heat of vaporization* and *sensible heat* are somewhat outdated and are no longer found in modern thermodynamics texts. In the interest of completeness, however, they will be defined here.

The latent heat of vaporization, sometimes called the enthalpy of vaporization, is the quantity of energy required to completely vaporize a unit mass of a saturated liquid at a given temperature and pressure. It is equal to the difference in the saturated vapor enthalpy and the saturated liquid enthalpy at the given pressure and temperature and is tabulated in the steam tables as h_{fg}.

Sensible heat is the quantity of energy required to increase the temperature of a unit mass at constant pressure from the saturated vapor state to a given higher temperature. It is calculated as the enthalpy change between the two states.