2.6 REPRESENTATION OF SUBSTANCE PROPERTIES

2.6.1 SOLID, LIQUID, GASEOUS PHASES

A pure substance can be in one or more of three phases: solid, liquid or gaseous. Solid state may even include several varieties known as allotropic, which reflect the different possible arrangements of the crystal lattice.
These three phases are distinguished, at the microscopic level, by the intensity of intermolecular forces. In the solid state, they allow atoms only to oscillate around fixed positions randomly distributed or ordered (crystal).
Their intensity decreases in liquids, which have no proper form, but remain slightly compressible. This is called a short distance order and disorder at long range. In a gas, intermolecular forces are very weak and the molecules move in an erratic motion.

When heating a solid at a well chosen constant pressure, it turns into liquid, and we talk of fusion. If we continue to provide heat, the liquid turns to vapor, and we talk of vaporization. It is also possible that a solid turns directly into vapor, which is called sublimation. The temperature at which these changes are realized depends on the pressure exerted on the substance considered. For example at atmospheric pressure, the CO_2 sublimes, that is to say, goes directly from solid to gaseous state, while water boils at 100 °C.
When a given mass of a pure substance is present in a single phase, its state is defined by two variables, for example its pressure and temperature. In the (P, T) plane, the three phases correspond to three areas, separated by three saturation curves (sublimation, vaporization and fusion) joining at the triple point T (Figure 2.6.1).

Each curve corresponds to a two-phase equilibrium. For example, the rightmost curve is the set of points representing the equilibrium of a liquid with its vapor. The two-phase equilibrium assumes that the pressure and temperature satisfy a relationship characteristic of the nature of the fluid.

For each of these phase changes to happen, it is necessary to provide or absorb energy, called latent heat of change of state. During the change of state, there are significant variations in the specific volume, except for fusion-solidification. This is particularly the case during vaporization, vapor being about

Figure 2.6.1: Phases of a substance

600 to 1000 times less dense than the liquid. This change in specific volume occurs at constant pressure and temperature.

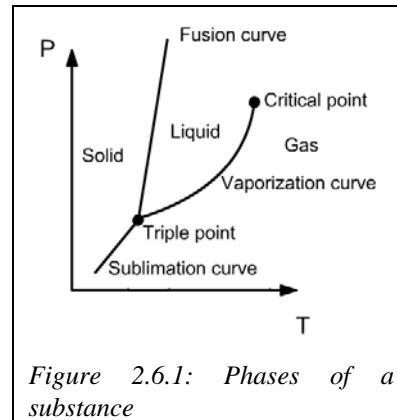Let us give some examples illustrating either the practical use of phase changes, or the constraints induced by the presence of a liquid-vapor equilibrium:

• When adding ice cubes to a warm drink, we provide heat which melts them, which cools it. As the latent heat of fusion of ice is much larger than the heat capacity of the drink, we get the desired cooling effect without bringing too much water dilution;

• To transport methane over long distances by sea, it is liquefied at a temperature of - 160 °C, reducing its specific volume 600 times with respect to gas. It is thus possible to maintain atmospheric pressure in the tanks of the LNG ship. Although these tanks are very well insulated, you cannot avoid some heat exchange with the surroundings, which has the effect of vaporizing a small amount of gas which is used for propulsion;

• In contrast, butane or propane gas distributed for culinary purposes is confined in a liquid state at room temperature in thick metal cylinders, in order to resist the inside pressure of a few hundred psi or tens of bar;

• All cooking done in boiling water takes place at 100 °C if the pressure is equal to 1 atmosphere, and this irrespective of the thermal heat supplied to the cooking. Thus we can define the precise duration for cooking a recipe, for example, a boiled egg;

• The principle of the pressure cooker is to overcome this limit of 100 °C by doing the cooking in a chamber at a pressure exceeding 1 atm. It can reach 110 °C and 120 °C, in order to cook food more quickly;

• An example of condensation is that which is deposited on cold surfaces in contact with moist air, like mist on a window, or the morning dew on leaves.

The triple point corresponds to the state where it is possible to simultaneously maintain equilibrium between all three phases. The critical point represents the state where the phase of pure steam has the same properties as the pure liquid phase. At higher temperatures and pressures (supercritical), it is not possible to observe a separation between liquid and gas phases: the disk surface which separates the liquid and vapor phases disappears at the critical point.

In practice, in heat engines, the working fluid is most often in the gaseous or liquid state, or as a mixture of gaseous and liquid phases. To calculate their properties, one is led to distinguish two broad categories of fluids: the ideal gas, which can be pure or compound, which includes the perfect gas, and condensable real fluids, which can also be pure or compound.

In Thermoptim all these types of fluids are represented, with the exception of mixtures of real fluids, which can however be taken into account through external mixtures, as explained in Chapter 1 of Part 4. In what follows, we will successively deal with ideal gases, their mixtures, liquids and solids, properties of a mixture of phases in liquid-vapor equilibrium and condensable real fluids. We conclude with the study of moist mixtures of dry gas with water vapor, of real fluid mixtures and of charts used in absorption cycles.

2.6.2 PERFECT AND IDEAL GASES

Many thermodynamic fluids in the vapor phase may be treated as ideal gases in a wide range of temperatures and pressures. This requires that the temperature-pressure combination deviates from the condensation zone as much possible (that is to say that the pressure is not "too" high or the temperature "too" low). Such conditions are commonly the case for gases known as "permanent" at ambient temperature and pressure, such as hydrogen, oxygen, nitrogen, the oxygen-nitrogen mixture that is dry air etc. Even the water vapor in the atmosphere behaves almost like an ideal gas as its partial pressure remains moderate.

The ideal gas model is based on the assumption that the molecular interactions in the gas can be neglected, except for collisions between them. The kinetic theory of

gases can then explain the gas macroscopic behavior from mechanical considerations, and statistics on the movements of its molecules.

The fundamental assumption of ideal gases is that their internal energy (and their enthalpy) is independent of pressure. Given that all real gases can be liquefied, there is rigorously no ideal or perfect gas. These concepts are fundamental, however, because the practical determination of the state of a real fluid is always made by reference to the corresponding ideal or perfect gas, which approximates the behavior at very low pressure and/or high temperature.

Specifically, to represent the state of a fluid, a cascade of increasingly complex models is used depending on the desired accuracy, the simplest being that of the ideal gas, the most elaborate corresponding to real fluids.

2.6.5 LIQUID - VAPOR EQUILIBRIUM OF A PURE SUBSTANCE

In compressible fluid machines it is often necessary to study the processes bringing the fluid into the liquid state. The ideal gas to zero does not exist, all fluids being condensable, and it is necessary to know their properties in the liquid state.

The study of vapor-liquid equilibrium is based on the law of phase mixture or lever rule that merely reflects the extensiveness of state functions with the assumption that the interfacial energy is negligible, which reads: volume, internal energy, enthalpy, entropy of a phase mixture, at pressure P and temperature T, are respectively the sums of these properties in the different phases constituting the mixture, taken in isolation at the same pressure and at the same temperature.

On various thermodynamic charts presented below, the vaporization or vapor-liquid equilibrium area is evident for temperatures and pressures lower than the critical point. This area is bounded on the left by the saturated liquid curve, and on the right by the dry saturated vapor curve. These two curves define the saturation curve, whose shape is characteristic. Between these two curves, pressure and temperature are no longer independent: they are connected by a relationship known as saturation pressure law or vapor pressure law, and the system is mono-variant.

2.6.6 REPRESENTATIONS OF REAL FLUIDS

The increase in pressure and/or lowering of the temperature can justify a reconsideration of the ideal gas equation (2.6.1). This is especially the case near the liquid-vapor equilibrium zone.

When the fluid no longer satisfies the ideal gas equation, its internal energy and enthalpy are no longer based solely on temperature.
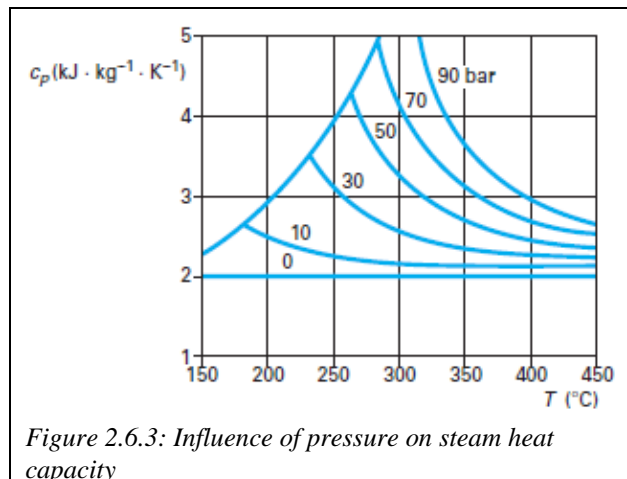

Figure 2.6.3: Influence of pressure on steam heat capacity

This behavior is shown in Figure 2.6.3, for superheated steam. It is clear that the heat capacity c_p of this substance is the more affected by the pressure as it is higher and the temperature is lower (that is to say, especially in the immediate vicinity of the saturation curve).

To determine the state of a real fluid, we use most often a thermodynamic chart, a table of thermodynamic property values, or a set of equations of state covering the various zones necessary.

Traditionally, thermodynamic charts are the most used. There has however been a marked evolution of the practice, the development of micro-computers making possible the direct calculation of fluid thermodynamic properties in a wide range of variation of state variables. Thermoptim allows us to make such calculations precisely.

However, even if one has a fluid properties computer, charts retain a strong interest to provide education, because they can easily view the real gas properties, including the liquid-vapor zone. We therefore begin by presenting them.

Moreover, the usual diagrams are increasingly computerized, which allows us to conciliate ease of use due to graphical display and numerical accuracy. Interactive charts of the Thermoptim family, based on the same equations as the software, are one example. These diagrams, shown in Figures 2.6.7, 2.6.8, 2.6.11 and 2.6.12 are available from the demo version of Thermoptim, their interactivity being deactivated. The reader interested in their construction may in particular display only some of the isovalue curves, by selecting them in the View menu.

2.6.6.1 Thermodynamic charts of pure substances

A pure substance of given mass being a bivariant system, its state can be represented on a 2 axes chart, on which are plotted a number of iso-values or "contours".

Among the many possible coordinate systems, we will retain four:

- the Clapeyron chart (P, v) which gives the most direct image of the mechanical processes, but is little used for the study of industrial projects, because it does not allow one to accurately read the usual energy quantities, including entropy and enthalpy;

- the entropy chart (T, s) that directly visualizes the reversible heat transfers ($\int Tds$) and the various possible irreversibilities;

- the Mollier chart (h, s), which is a change of the former, intended to directly show the energy transfers in an open system, which has the advantage that the enthalpy involved can be read without difficulty;

- the (h, ln(P)) chart, with enthalpy as abscissa and pressure as ordinate (usually with a logarithmic scale to cover a wide range of values). This chart is traditionally used in the study of cycles running in reverse (heat pumps or refrigeration). Its interest is to combine the essential mechanical constraint (P) of compressors to the energy variable (h);

- exergy charts (or usable enthalpy charts) (h, x_h) and (s, x_h), with the enthalpy or entropy as abscissa and exergy as ordinate, allow one to view exergy brought into play in processes, and therefore lend themselves well to the study of irreversibilities taking place in cycles.