## 3. Phase behavior of single component systems

*Figure 3-1 All phases in Yellowstone*

You may also want to check out the following website: [http://www.eng.usf.edu/~campbell/ThermoI/Proptut/tut1.html](http://www.eng.usf.edu/~campbell/ThermoI/Proptut/tut1.html)

The purpose of this chapter is to introduce the relationships between pressure, specific volume and temperature for single component (or pure) systems. This relationship can be illustrated using a 3D phase diagram in which all possible phase states are shown. OF course in petroleum engineering, we are really interested in multi-component systems, but a thorough knowledge of single component behavior will help in understanding the more complex behavior of multi component systems.

Note that pure means the substance is composed of one chemical species, but this species can occur in various states with different physical structures (solid, liquid, gas), and several phases may be present at the same time.

### 3.1 The PVT diagram

Not all intensive properties are independent. For a pure substance existing in the form of a single phase specifying two intensive variables will fix the value of all others. Therefore, we can think o f pressure, specific volume and temperature as forming a relation (the PVT relation) between two independent variables and a dependent one. This relation can be depicted as a surface in three-dimensional space. Each point on this surface this represents a naturally occurring state. States outside the surface do not occur in reality.

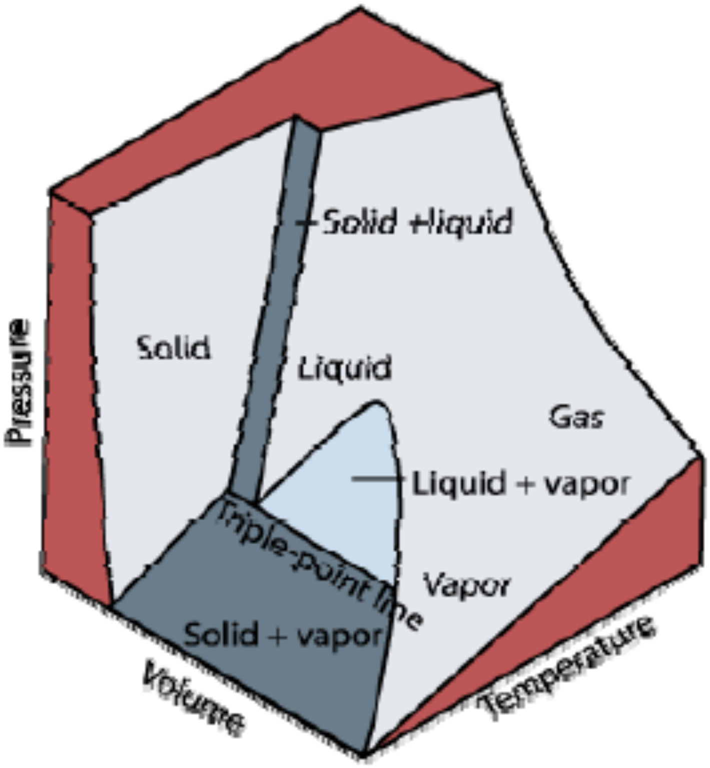
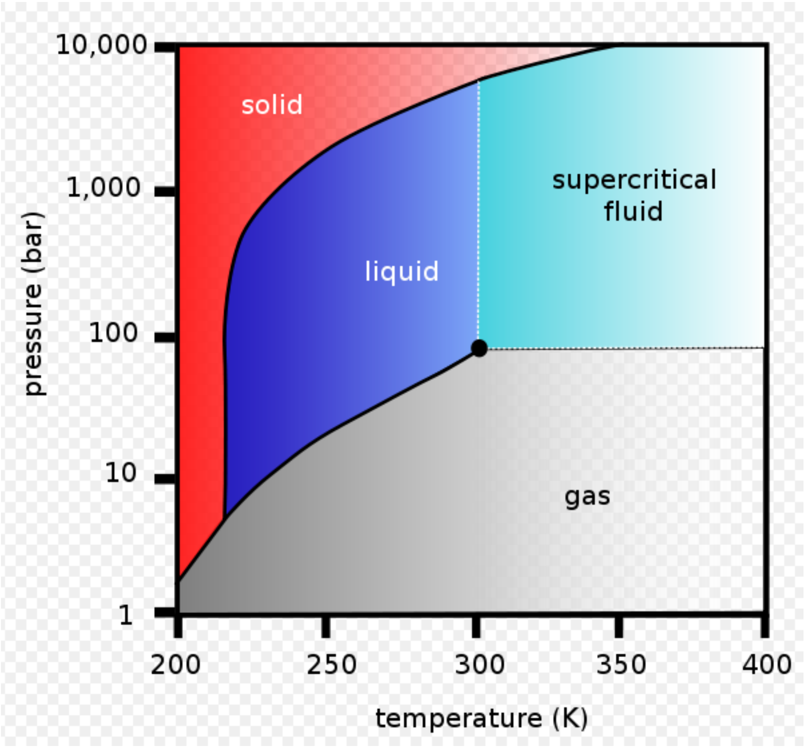


*Figure 3-2 The PVT surface*

Instead of the 3D surface, often the projections of this surface of planes of constant pressure, temperature or volume used. If we project onto planes of constant pressure (slice the surface at fixed heights) and put all intersecting lines (isobars) together in one picture, we get a VT diagram. If we project onto planes of constant volume, we obtain the PT diagram and a projection onto a place of constant temperature gives a PV diagram. We discuss the PT and PV diagram in detail below.

### 3.2 The PT diagram

The red line in the PT diagram below is the vapor pressure curve. Each point on this curve corresponds to one particular state in the two-phase vapor-liquid region. The pressure at such a point is called the vapor pressure at the corresponding temperature T, and the temperature at this pint is the boiling temperature at the corresponding pressure P. The diagram does not give any information about where inside the two-phase region this state lies – it could be saturated liquid, saturated vapor or any of the infinite number of mixture of liquid and vapor that exist.



The vapor pressure curve terminates at the critical point (purple dot). This point marks the highest temperature ($T = T_c$) and highest pressure ($P = P_c$) for which vapor and liquid can coexist. This definition is however not generalizable to multicomponent systems and therefore we will use the classical definition, which says that the critical point is that state of pressure and temperature at which the intensive properties of the gas and liquid are continuously identical. The other end of the vapor pressure curve is marked b the triple point (black dot). At the corresponding pressure and temperature, all phases coexist.

The black line in the figure is the melting curve. It gives the melting temperature as a function of pressure or melting pressure as a function of temperature. Note that for water, which is not contracting as it freezes, the slope of this line is negative rather than positive. The upper limit of the melting curve has not been obtained experimentally. The green line is the sublimation curve and provides the one-to-one relationship between temperature and pressure in the solid-vapor coexistence region. Theoretically, this line extends to a temperature of absolute zero and a pressure of absolute zero.

*Give an example of a substance that passes directly from solid to vapor (sublimes) without forming a pool of liquid at atmospheric pressure.*

The single-phase liquid region is located between the melting curve and the vapor pressure curve. The single-phase region is located below the sublimation and vapor pressure curves and terminates at the critical pressure. The single-phase solid region is located to the left of the melting curve. The supercritical fluid region is located for temperature above $T_c$ and pressure above $P_c$.

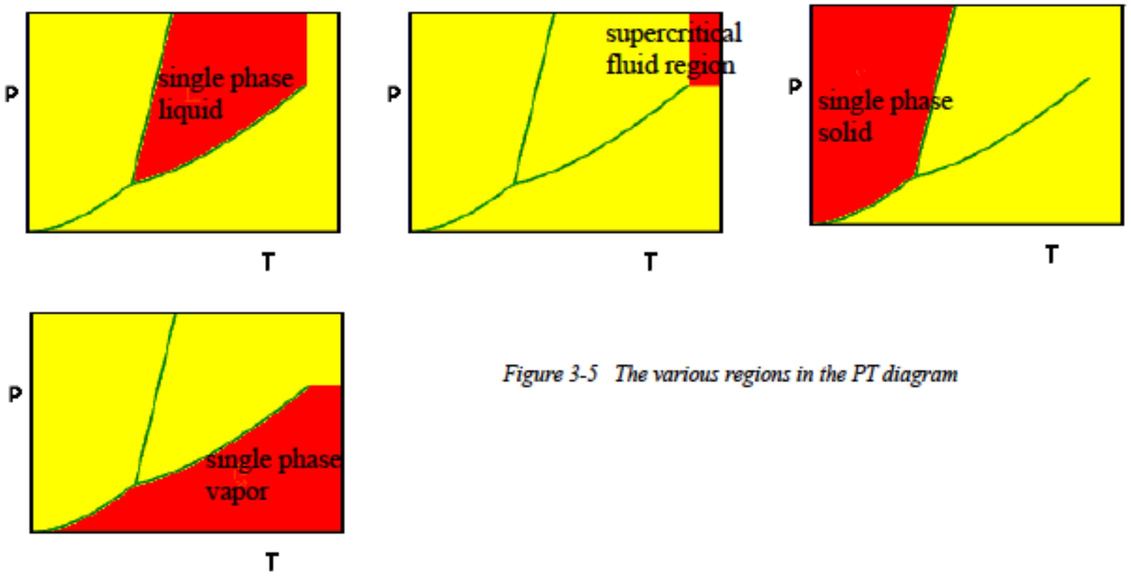


*Figure 3-5 The various regions in the PT diagram*

It follows from the above that the state of a substance is determined by the pressure and temperature at which that substance exists. Let's do an experiment. Suppose that we are in point A in Figure 3-6. The material is in the liquid state and the pressure is higher than the vapor pressure. If we decrease the pressure at a constant temperature (by expanding the volume) as shown by the black arrow in Figure 3-6, we will eventually hit the vapor-pressure curve. The pressure here is the vapor pressure at which point gas beings to form. As we further expand, the volume of gas increases and the volume of liquid decreases, but the pressure stays constant and we remained stuck in the intersection point of the black arrow and the vapor-pressure curve. Once the liquid disappears further expansion of the volume cause a decrease in pressure as the gas expands until we reach the end point of our path. This process is also illustrated in figure 3-7.

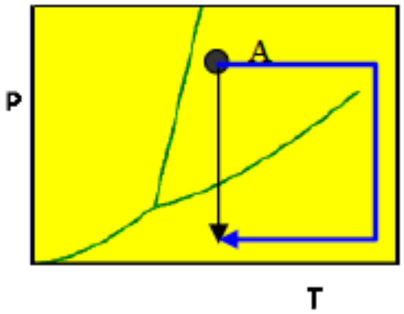


*Figure 3-6 Phase changes*

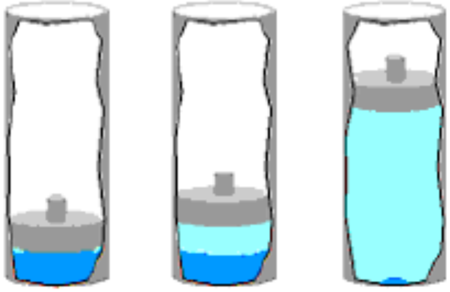


*Figure 3-7 Expansion*

But if we go to the same endpoint following the blue pat in Figure 3-6, we never pass the vapor pressure curve. The change from vapor to liquid occurs continuously in the supercritical fluid region and we never see any phase discontinuities.

## Clausius-Clapeyron Equation

The Clausius-Clapeyron equation expresses the relationship between vapor pressure and temperature, representing a mathematical expression of the vapor-pressure curve. Thermodynamic theory gives use the Clapeyron equation:

$$\frac{d_{p_v}}{dT} = \frac{L_v}{T(V_{mg} - V_{ml})}$$

The relationship $\frac{d_{p_v}}{dT}$ is the rate of change of vapor pressure with temperature, and therefore the slope of the vapor pressure curve. $L_v$ is the heat of vaporization of one mole of liquid, T the absolute temperature and $V_{mg} - V_{ml}$ the change in the volume of one mole as it goes from liquid to gas.

*Convince yourself that this equation makes sense: First check that it is dimensionally correct. Second, convince yourself that the slop should indeed be inversely proportional to the temperature. Now check the proportionality to heat of vaporization and volume change.*

As, generally, $V_{mg} >> V_{ml}$, we can write:

$$\frac{d_{p_v}}{dT} = \frac{L_v}{TV_{mg}}$$

*When is the above assumption not true?*

Using the ideal gas relation (see Lecture 8), $P_v V_{mg} = RT$, we get:

$$\frac{d_{p_v}}{dT} = \frac{p_v L_v}{RT^2}$$

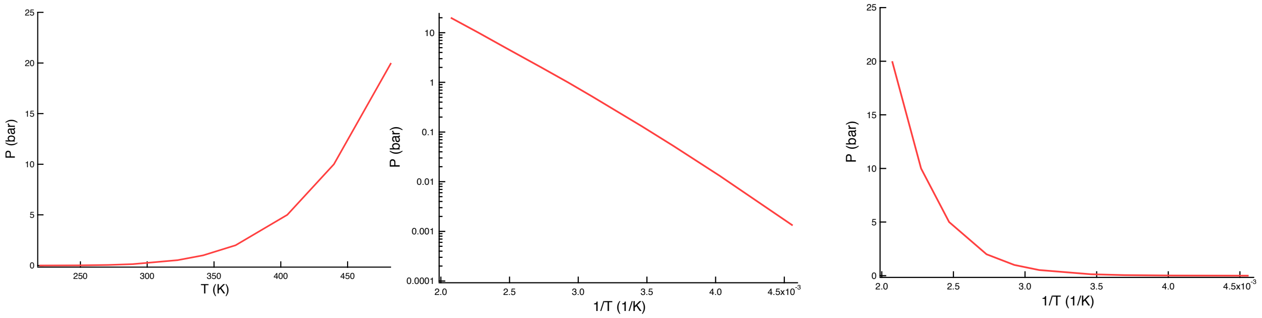
which is known as the Clausius-Clapeyron equation. If $L_v$ is constant, we can integrate the equation to give

$$\ln(p_v) = -\frac{LV}{R}\frac{1}{T} + C$$

where C is an integration constant, or:

$$\ln\left(\frac{p_{v1}}{p_{v2}}\right) = -\frac{LV}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

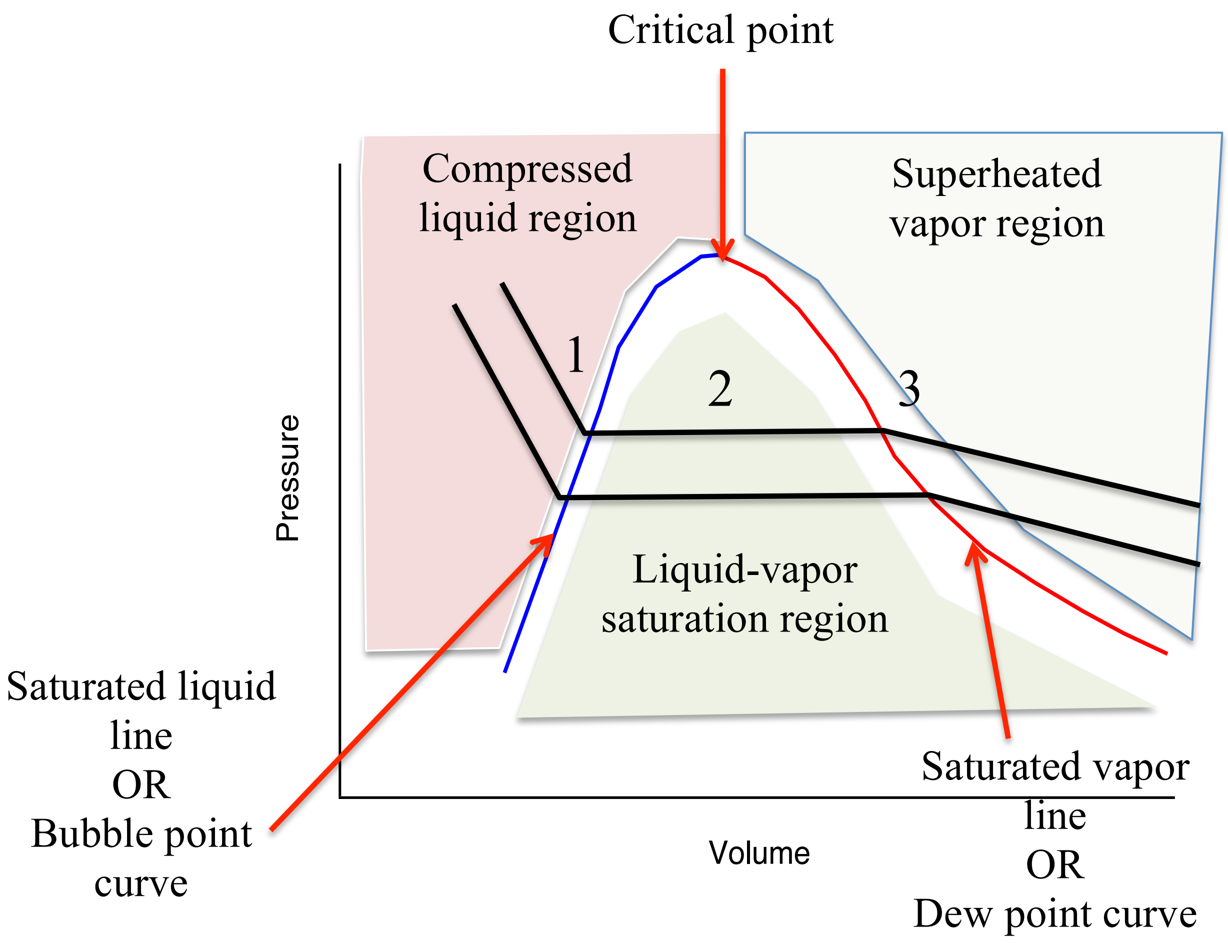
So if we plot the pressure against the reciprocal of the temperature on a semi-logarithmic plot, we expect to see a straight line. In reality, the line will be slightly curved over a long temperature range, as is evident in the vapor-pressure graph of n-hexane in Figure 3-7.



*Why would we expect a slightly curved graph over a long temperature range?*

### 3.3 The PV and density-T diagrams

Sometimes it is convenient to use a PV diagram instead of a PT diagram. Figure 3-8 shows a PV diagram with the various lines interesting points and regions.



The saturated –liquid line is also called the bubble point line (points at which gas bubbles are formed first). The saturated-vapor line is also called the dew point line (points at which drops are formed first).

*Looking at the isotherms, in what direction does the temperature increase?*

In the two-phase region between the bubble-point and the dew-point curves, vapor and liquid coexist in equilibrium. At point 1 on the bubble-point curve, the substance has the properties of a liquid. At point 3 on the de-point curve, the substance has the properties of a liquid. At point 3 on the dew point curve, the substance has the same pressure and temperature as in point 1 but is now a vapor. At point 2, the material consists of two distinct phases: one has the density specified by point 1, and the other then density specified by point 3. The specific volume at 2 is determined by the relative quantity of liquid and vapor present. We can write:

$$\left(\frac{W_L}{W_g}\right)_2 = \frac{length\ from\ 2\ to\ 3}{length\ from\ 1\ to\ 2}$$

From this it is clear that the state of the material can be specified completely by the pressure and specific volume. In the PT diagram, the state can only be determined completely outside the two-phase region (the vapor-pressure curve). This is the important difference.

Finally we have a look at a density-temperature diagram, shown below.

Again we look at a point 2 in the two-phase region. A liquid with density given by point 1, and a vapor with density given by point 3 are in equilibrium in this point. Note that as the critical point is approached along the dew-point curve, the density gradually increases. Along the bubble-point curve, the density of the liquid gradually increases, approaching the same value as the vapor at the critical point.

For pure components, the critical point can be determined by plotting the arithmetic average of the densities of the vapor and liquid defined at the pressures and temperature of the vapor pressure curve. This line passes through the critical point as illustrated in the above picture. The critical point can this be defined by the convergence of the vapor, liquid and average composite density curves.