

TA no. 4: Answers

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Question no. 1

Why do we need to compare the saturated pressure with the pressure given to know the phase of our system? Is there any physical intuition behind this?

Let us start with the saturated vapor pressure of water as a function of the saturated vapor temperature (see figure 1). Basically, we check how the saturated vapor temperature changes with the saturated vapor pressure (and vice versa). There is one point we know pretty well: at the atmospheric pressure (101.3 kPa), water boils at 100°C. So, let us start from the horizontal axis, at 101.3 kPa, and move towards the right on the same horizontal line (i.e., the same pressure at 101.3 kPa). At some point, our water will reach 50°C. However, at 101.3 kPa, we know that nothing happens, we still have a liquid phase. We need to keep moving on this line until we reach 100°C in order to get a saturated liquid vapor mixture. Then, we will keep adding heat to our system in order to raise the temperature above 100°C. Remember that during a phase change, the pressure and temperature of the system do not change. As a result, when the temperature goes beyond 100°C (for water at 101.3 kPa), we have a superheated vapor. The part on the left-hand side of the curve corresponds to the liquid phase and the part of the right-hand side to the vapor phase. All right, but why do we compare the saturated pressure with the pressure given?

So, we go to our tables and find the saturated pressure at 100°C for water – 101.3 kPa. The pressure given is lower than the saturated pressure (let us say 40 kPa). If we are at the point (100,101.3) and go down to (100,40), we see that we are in the right-hand side, which corresponds to superheated vapor.

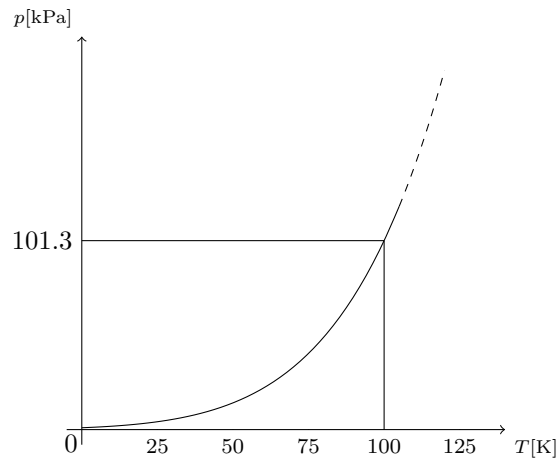


Figure 1: Saturated vapor pressure as a function of saturated vapor temperature for water

Looking at the figure is fine, but is there any better physical intuition for this? Let us look at the microscopic view (or molecular level). At the atmospheric pressure (101.3 kPa), water boils at

100°C, which means that the molecules are moving very fast and some of them overcome the intermolecular forces. The liquid-vapor mixture corresponds to groups of molecules (forming a liquid) and molecules far apart from each other (forming a gas). Let us now apply some pressure on our system (let us say 201.6 kPa). From the figure, we now that we are in the liquid phase (left-hand side of the curve). Does that make any sense? By applying pressure, we force our molecules to be closer to each other. The intermolecular forces depend on the distance between the molecules, so they become stronger. The gas molecules, moving about at random previously, will settle (forming a liquid). The reverse process is also true. When we decrease the pressure (lower than the saturated pressure), our molecules are further apart from each other and are able to overcome these molecular forces and break away (forming a gas).

The same idea works for the temperature (instead of the pressure). If the temperature is higher than the saturated temperature, we have a superheated vapor.

Question no. 2

What is the compressibility char?

The compression factor Z (or compressibility factor) quantifies the deviation from the ideal gas assumption and is defined as:

$$Z = \frac{pV}{nRT} \quad (1)$$

For ideal gases, $Z = 1$ such that $pV = nRT$. The ideal gas model assumes that the molecules do not interact between each other (which corresponds to low pressures and/or high temperatures). When we increase the pressure, the molecules are closer to each other and the attractive intermolecular forces must be taken into account. The volume being smaller than the ideal gas law model (due to attraction), $Z < 1$. If we compress our gas even more, compressed highly, repulsive intermolecular forces dominate, $Z > 1$.

The important fact here is that our ideal gas assumption is valid for Z close to 1. Gases behave differently at a given pressure and temperature, but have a similar behavior at pressures and temperatures normalized with respect to their critical temperatures and pressures. For this reason, we use the ratios, called reduced properties p_R and T_R , as follows:

$$p_R = \frac{p}{p_{CR}} \quad T_R = \frac{T}{T_{CR}} \quad (2)$$

where the critical pressure and temperature correspond to the pressure and temperature of the critical point (different from each substance). The closer a real gas is to its critical point, the larger are the deviations from the ideal gas model – since we are closer to a liquid phase (definitely not a perfect gas).

As a result, the compressibility chart gives Z versus P_R for various values of T_R in the same way a topographic map represents relief (contour map). The compressibility chart is an empirical (experimental) chart to predict the behavior of real gases – based on the Van der Waal equation:

$$\left[p + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT \quad (3)$$

Among the assumptions made for the ideal gas model, we have: (i) no interaction between molecules and (ii) molecules are so small that their volume is negligible.

If (i) is not true, the pressure goes down compared to the ideal gas law model. Since more interactions between molecules mean less collisions with the walls.

$$p_{measured} = p_{ideal} - a \left(\frac{n}{V} \right)^2$$

$$p_{ideal} = p_{measured} + a \left(\frac{n}{V} \right)^2$$

If (ii) is not true, the molecules have a volume. The total volume in which the molecules can move is smaller than expected by the ideal gas model:

$$V_{ideal} = V_{measured} - nb$$

The coefficients a and b are determined experimentally. All right, but how do we use the compressibility chart?

First, we calculate the reduced pressure and temperature using equation 2, where the critical pressure and temperature can be found in the tables. Then, we go to the compressibility chart and look for the intersection between p_R and T_R (that is, a point on the graph). The value on the horizontal axis of this point gives the compressibility factor Z (see figure 2, which is also defined as:

$$Z = \frac{\nu}{\nu_{ideal}} \quad (4)$$

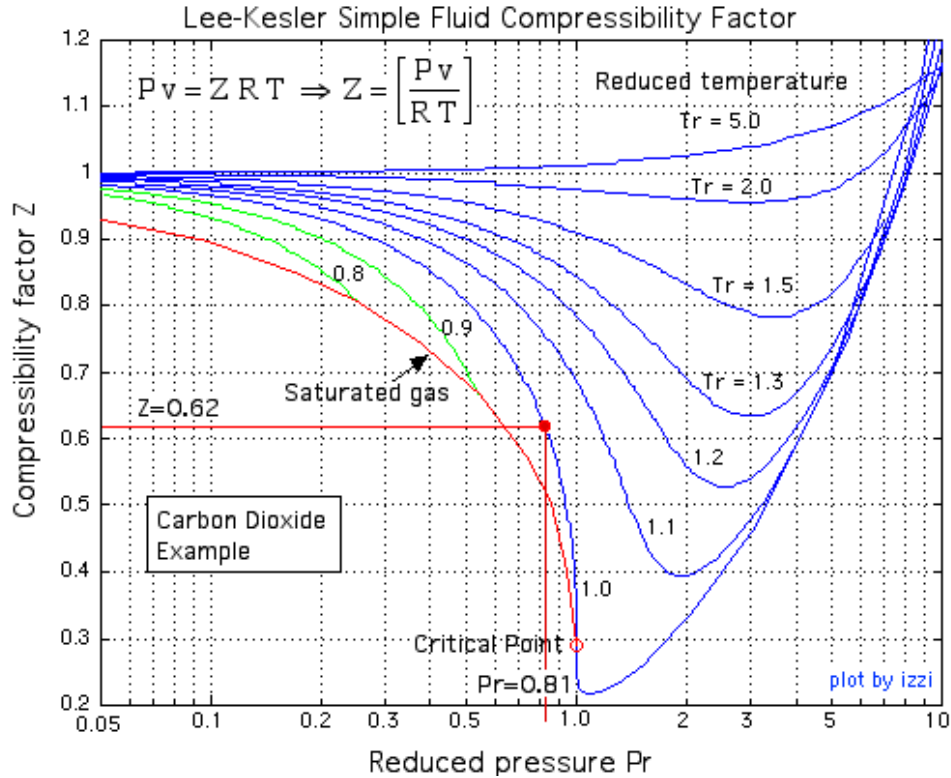


Figure 2: Example to find Z (from LINK)