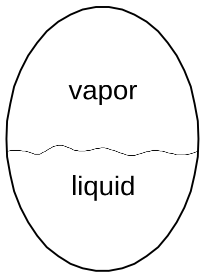
Phase Diagrams and the Triple Point

Consider an *isolated* (adiabatic) container of water at 100° C. This container has only water, in vapor and liquid form—no air, or any other substance.



In this container:

- The vapor is in equilibrium with the liquid; that is, if one watches the container, the amounts of vapor and liquid do not change.
- the vapor pressure turns out to be 1 atmosphere (760 mm of Hg).

Suppose that we reduce the temperature to 90° C. Will all of the water vapor suddenly condense to liquid? Obviously not, at least to anyone who has ever been in a steamed-up bathroom or who has experienced a hot July day.

In fact, it turns out that everything is much as it was before, except that the pressure is a little lower, and there is more liquid, and less vapor present. If we do an experiment in which we measure the pressure of the vapor as a function of the temperature, we obtain data similar to those shown below:

Temp (°C)	v.p.(mm Hg)
0	4.6
20	17.5
80	355
100	760
120	1520

In other words, we find that at any given temperature, the pressure of water vapor in *phase equilibrium* with liquid water will have some definite, characteristic pressure.

Note also that when the temperature T = 100° C, the vapor pressure is exactly 760 mm Hg—which is just the standard atmospheric pressure (at sea level). It's not a coincidence—by definition, the *normal boiling point* of a substance is the temperature at which its vapor pressure is equal to the pressure of 1 atmosphere.

Let's see if we can make sense of this definition. What characterizes a boiling liquid? [long pause to think deeply!]

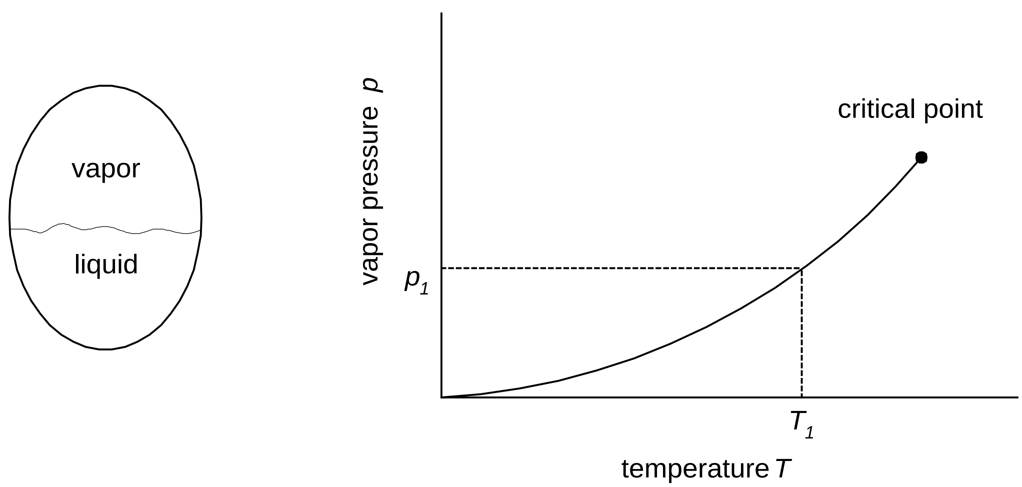
Consider a pan of water on a stove—**not** a closed system, like the one above. Well, when we turn on the heat, eventually it boils—bubbles form. What is inside those bubbles? Not air—we can put pure water, with no dissolved air, in a pan, and it still bubbles away when its temperature reaches the boiling point. So the bubbles must contain water vapor. Why do not bubbles form at lower temperatures? [another long pause to think]

Well, perhaps they start to form; but the atmosphere is exerting a pressure—that is, pushing down—on the surface of the water, with (of course) atmospheric pressure. Suppose the water is at 20° C—its vapor pressure, according to our table, is only 17.5 mm Hg. What would happen to a bubble that tried to form, with the atmosphere pushing down at around 760 mm Hg? Right! But at 100° C, the vapor pressure of water can sustain itself against the atmosphere—and so bubbles can form!

Questions to ponder:

- Why does water boil at a lower pressure in the mountains, at higher altitudes?
- How does a pressure cooker work?
- Is there anything fundamental about the boiling point of a substance?

We can put this information together in a *phase diagram*, which is a graph of vapor pressure versus temperature. It will look something like this:



The curve is the line of *phase equilibrium* between the liquid and vapor phases; thus, p_1 is the vapor pressure at temperature T_1 for a system in which liquid and vapor are in equilibrium in a closed container.

Aside: Note the presence of the *critical point*—it turns out that the liquid-vapor equilibrium curve does not go on forever, but stops, at a pressure and temperature that is characteristic of a given substance. Here are a few examples:

substance	critical temp (K)	critical pressure (MPa)
water	647.07	22.05
CO_2	304.14	7.375
Nitrogen	126.2	3.39

remember that
1 Torr = 1 mm Hg = 133.32Pa
1 MPa = 10^6 Pa
temperature conversion: temperature in K = °C + 273.15
1 atmosphere = 0.1013 MPa

data are from Zemansky and Dittman,
Heat and Thermodynamics (7th ed)

Note that this description of water fits into our everyday experience:

- On a cold day, just above freezing, a small puddle of water evaporates slowly—why?
- On a warm day, the same puddle evaporates much more quickly—again, why?

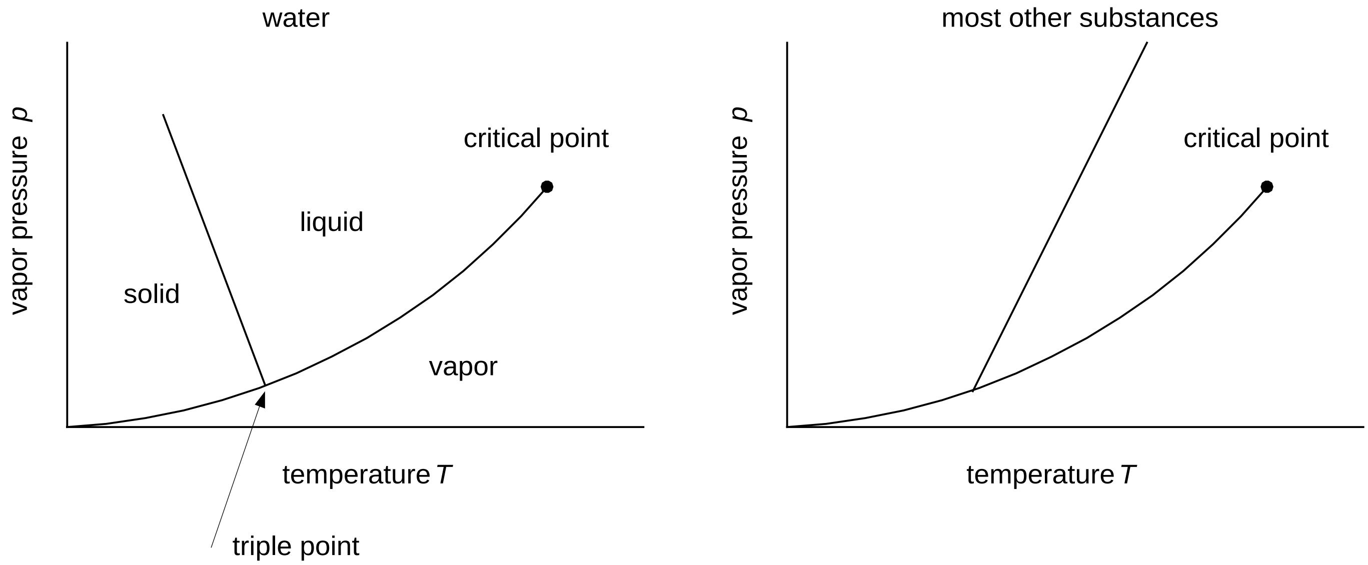
Let's think a little more carefully about what goes on when the water in our sealed flask changes temperature. When we reduced the temperature from 100° C to 90° C, we must have done something like the following:

- We place the flask in contact with some object (a pan of water, for example) at a lower temperature.
- Heat flows from the flask to the water in the pan (translation: energy moves from the flask to the water in the pan as a result of a temperature difference).
- In the process, some of the vapor turns into liquid.

It is the last step that interests us here. Apparently the energy lost by the flask comes from the vapor; and as a result of losing that energy, some of the vapor turns into liquid.

We call such a gain or loss of energy, which can take place at constant temperature, a *latent heat*, or sometimes, a *heat of transformation*; we will say more about them later on. For now, note that when a pot of water boils, what happens is that the heat from the burner is absorbed by liquid water; as it absorbs the latent heat, the water is transformed into vapor (bubbles), which rise to the top and disperse. This process takes place, of course, at a constant temperature.

So far, we have talked about the vapor and liquid phases. If we consider solids, the phase diagram looks something like this:



There are several points to note here:

- There is a latent heat of vaporization for phase transitions between the liquid and gas phases, and latent heat of fusion for phase transitions between the liquid and solid phases; there is also a latent heat for transitions between the vapor and solid phases.
- For most substances, the slope of the liquid-solid phase equilibrium curve is positive. For water, the slope is negative. It is worth considering the implications of that difference.

We are finally in a position to define the *triple point* — it is just the point at which the two phase equilibrium lines intersect. All substances except helium have triple points. Note that unlike the freezing and boiling points, which depend on external pressure, the triple point is fundamental. When you see a closed container, in equilibrium, that contains solid, liquid, and vapor, you are assured that the substance is at its triple point—a few examples are given in the table. Since triple points are fundamental, they are often convenient for defining temperature scales.

Triple Points		
substance	**Temp (K)**	**Pressure (kPa)**
water	273.16	0.612
CO_2	216.6	518
nitrogen	63.15	12.46

data are from Zemansky and Dittman, *Heat and Thermodynamics* (7^{th} ed); note that the triple point of water is 273.16 K = 0.01° C, slightly above the normal freezing point.