

6.4: Gas, Vapour, Liquid and Solid

Our description of the behaviour of a real substance in section 6.2 was incomplete in many ways, not least because it made no mention of the solid state. At very low temperatures or at very high pressures, most substances will solidify

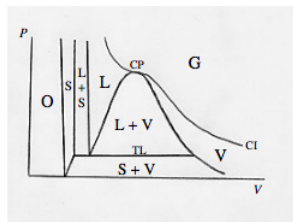


FIGURE VI.3

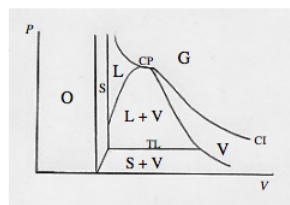


FIGURE VI.4

In figures VI.3 and 4 I have sketched schematically, by hand, the several regions in the PV -plane in which a substance exists in its several stages. Unlike in Figure VI.1 and VI.2, I have not drawn *isotherms*. The various lines are intended to represent the boundaries between phases, and are therefore more akin to the dashed curves in figures VI.1 and VI.2. The one exception is the critical isotherm, CI, which is indeed the curve that separates gas from vapour or liquid, but which is also, of course, an isotherm. The difference between figures VI.3 and VI.4 is that figure VI.3 represents a substance that expands when it melts from solid to liquid, while figure VI.4 represents a substance that contracts when it melts from solid to liquid (that is, the solid is less dense than the liquid, and will float upon it.) Most substances expand upon melting, but we have to include those exceptional substances that contract upon melting, because one such substance is one of the most important of all – water.

You can try to understand the figures a little by moving along a horizontal line (isobar) or along a vertical line (isochor) and noticing where phase changes take place. Can you see, for example, where a solid will change to a vapour without going through a liquid phase (sublimation)?

You will note, in the figures, the *critical isotherm* CI, that separates gas from liquid or vapour, and you will note that, at temperatures above the critical temperature, the only phase possible is *gas*, and the substance cannot be liquefied merely by compression. You will note also the *critical point* CP. You will also see the *triple line* TL, along which solid, liquid and vapour co-exist together. What of the region marked O? The substance cannot exist here in solid, liquid or gaseous phase. To that extent, we see that the van der Waals equation may be a little bit better than we thought it was, because you will remember that it went up to infinity at a third of the critical volume. All that this means is that by then the molecules are so tightly jammed together that you simply cannot compress them any further. Although a substance cannot exist in an ordinary solid, liquid or gas phase in the region marked O, if the matter is *degenerate* it will be in this region. The electron structure of the atoms breaks down, so that it then does become possible to jam the atoms closer together. This may mean something to those of you who are familiar with the concept of degenerate matter. If you have not heard of it, do not worry; you are unlikely to come across it unless you visit a white dwarf star, or the core of a massive star, or have to take an examination in astrophysics. For the time being, we shall look the other way and pretend it doesn't exist.

We can get a little more insight by looking at the PT -plane. Figure VI.5 shows a substance that expands on melting, and figure VI.6 shows a substance (such as water) that expands on freezing. In the PT -plane, the *triple point* (where solid, liquid and vapour) are in equilibrium with each other, appears as the *triple point*, TP. (In PVT -space it is a *line*, although the critical point CP remains a genuine point in PVT -space.) The line separating liquid from vapour terminates at the critical point, and the line is often drawn as though it were somehow left hanging in mid-air, so that one is uncertain whether a given point near the critical point represents a gas, a vapour or a liquid. But in the PT -plane, the critical isotherm is a vertical line (shown as dashed in the figures), and the liquid/vapour boundary terminates at the critical isotherm, and there is no question what phase is represented by a point near to the critical point. To the right of the critical isotherm, we have a gas. To the left, we have either a liquid or a vapour, depending on whether we are above or below the liquid/vapour boundary. As we cross the solid/vapour boundary, below the critical temperature and below the critical pressure (on Mars!) we have a phase change directly from solid to vapour or vapour to solid – i.e. sublimation.

(I have often heard that, below the triple point, a solid will "sublime". I think I prefer the verb "to sublimate".)

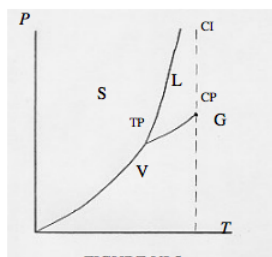


FIGURE VI.5

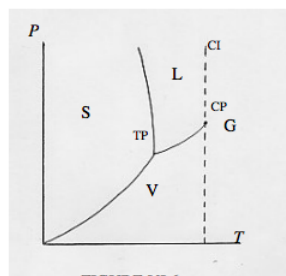


FIGURE VI.6

Really to appreciate these diagrams you need to see and to handle a three-dimensional model in 3- space. My skills at making drawings with my computer are nowhere near good enough yet for me to attempt a three-dimensional drawing, but Mr Charles Card of the University of Victoria was kind enough to photograph for me a model from the University's collection, and I reproduce these below as figures VI 7,8 and 9.

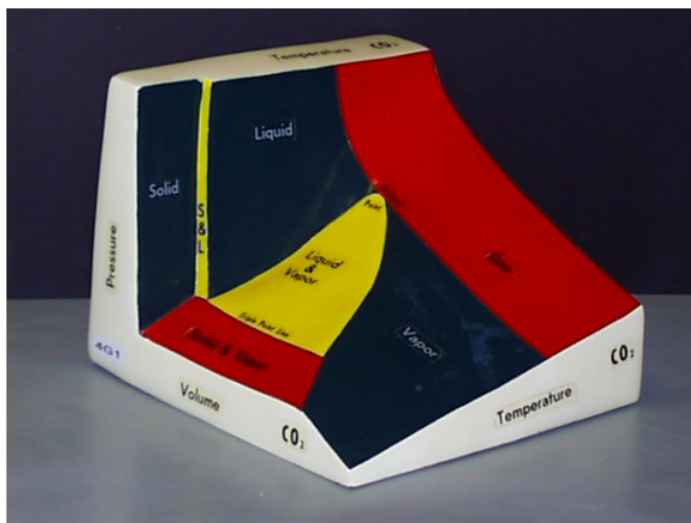


FIGURE VI.7

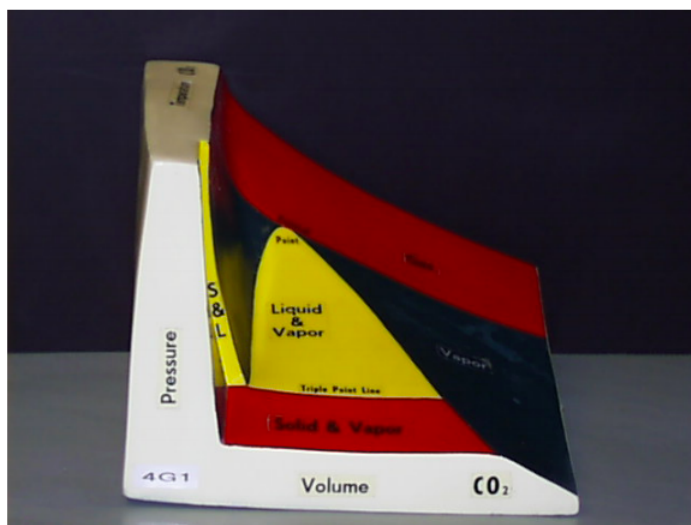


FIGURE VI.8

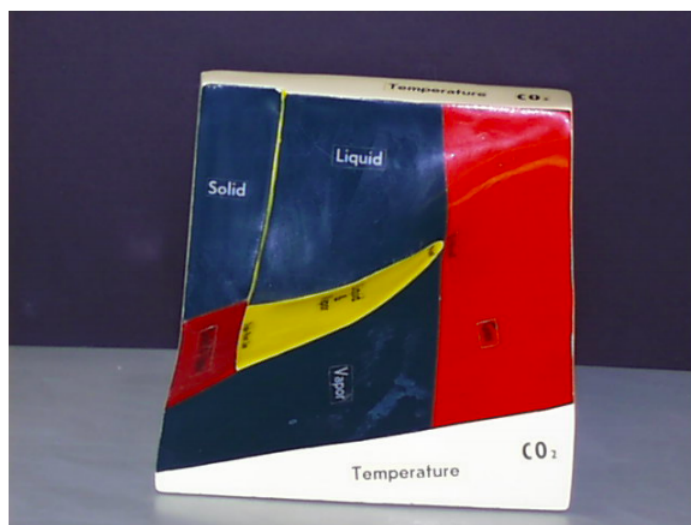


FIGURE VI.9

I now give some numerical values for the critical temperature and pressure, the compression factor, and the temperature and pressure of the triple point for H_2O and for CO_2 . These are not intended as definitive values. I looked them up in a number of sources and I found a surprisingly wide range of the numbers quoted. They are given here merely to give the reader a rough idea of what the values are for these two substances. The temperature quoted for the triple point of H_2O is, of course, exact, being one of the fixed points of the Kelvin scale. Recall that one atmospheric pressure is about $1.01 \times 10^5 \text{ Pa}$.

The reader might like to see whether these numbers are compatible with the numbers I gave for the van der Waals constants in Section 6.3. Exact agreement is not to be expected, because the figures I quote are only approximate and are gleaned from a variety of sources and also, of course, neither gas can be expected to obey van der Waals' equation exactly. If the numbers seem to be wildly discrepant, please let me know.

We who live on the surface of Earth are familiar with water in its solid, liquid and vapour forms, and this might suggest that the conditions on the surface of Earth, the temperature and pressure, must be close to the triple point of water. We see from the above table that the triple point of water (which is defined to be $273.16 \text{ K} = 0.01^\circ \text{C}$ in the International Temperature Scale), is indeed near our typical ambient temperatures, but the triple point pressure of water is 611.73 Pa , which is only about 0.006 atm . However, we are near the triple point if the partial pressure of water vapour in the atmosphere is close to 0.006 atm , which it often is. So we are indeed close to the triple point, which is why we so often see water in its three phases. Incidentally, the $P : T$ diagram for the water system is a good deal more complicated than the ideal diagram of figure VI.6, particularly in the "solid" region, since there are apparently many (about 15) different forms, or phases, of water ice.

Some idle thoughts on vapours. There is a question of how to spell "vapour". In the United States, "vapor" is usual, and in the United Kingdom "vapour" is usual. "Vaporize" is a bit trickier. The spelling "vaporize" is usual in the United States, but what to do in the United Kingdom? Is it vapourize, vapourise, vaporize or vaporise? Is there a u or no u? Is it z or s? To answer the first question: In the United Kingdom, the u, as in the United States, is omitted. Only weak spellers and those who would try to be "more English than the English" would try to insert a u. As for s or z, either seems to be used in the United Kingdom. Etymologically, z would be the better choice, so the spelling "vaporize" is perfectly acceptable on both sides of the Atlantic Ocean.

More idle thoughts on vapours. Is a "vapour" a "gas"? What is a "fluid"? And is glass a liquid? Some authors treat "gas" and "vapour" as though they were quite different things: a gas is not a vapour, and a vapour is not a gas. Others regard a "vapour" as being a sort of gas – namely a gas whose temperature is below the critical temperature and which can be liquefied by increasing the pressure. In that case, what do you call a gas that is above the critical temperature? The term permanent gas is often used. Thus a vapour is a gas below its critical temperature, and a permanent gas is a gas above its critical temperature.

A *fluid* is something that flows. Thus liquids and gases (including vapours) are fluids. There is, you would imagine, always a clear distinction between a liquid and a gas. But is the distinction always so clear? I admit that I have never actually seen the phenomenon that I am about to describe, but it is described so often that I presume someone has seen it! Consider a closed container with a liquid in equilibrium with its vapour. The liquid and vapour are separated by a sharp, horizontal boundary. That is to say, the system is on the line separating liquid and vapour in figures VI.5 and 6. This line can be regarded, if you like, as a graph

of boiling point versus temperature, or equally of vapour pressure versus temperature. If you raise the pressure, the boiling point increases; or if you increase the temperature, the vapour pressure increases. More liquid will enter the vapour state, and, as the pressure of the vapour increases, so does its density. The liquid, on the other hand, is almost incompressible, and, because of thermal expansion, its density decreases. As we move up the line separating liquid from vapour in the $P:T$ plane, the density of the vapour increases and the density of the liquid decreases. Their densities become more and more equal until, as we approach the critical point, the boundary between liquid and vapour becomes less and less distinct, and less constrained by gravity to be horizontal, until eventually, at the critical point, the distinction between liquid and vapour blurs and ultimately disappears. So – what have you got then? It is certainly a *fluid*, but are you going to call it a gas, a vapour or a liquid? Since none of these words would seem to have a stronger claim than either of the others, some authors refer to the substance when a little above and to the right of the critical point in the $P:T$ plane as a *supercritical fluid*.

There is also the question as to whether glass is a solid or a liquid. A famous radio personality many years ago, on a “Brains Trust” programme broadcast by the British Broadcasting Corporation, Professor C. E. M. Joad, was famous for his sentence: “It all depends on what you mean by...” So I suppose the question as to whether glass is a liquid or a solid depends on what you mean by a liquid or a solid. The moment when I drop a tumbler and it shatters into many viciously sharp fragments is not a good moment to convince me that glass is a liquid. Those who assert that glass is a liquid say that it has not got a solid crystalline structure, and that it *flows*, albeit very slowly. It has a very large viscosity. We are told that windows in ancient mediaeval cathedrals are thicker at the bottom than at the top, as a result of the viscous liquid flow over the centuries. I don’t know if any of the many people who have told me that have actually personally measured the thickness of a cathedral window.

At any rate, before you started this chapter, you had a very clear idea in your mind about the differences between a solid, liquid and a gas. Now that I have painstakingly explained it all, you are completely confused, and are no longer at all sure that you know the difference.

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