Phase Transition

(Thermodynamics)

e-content for B.Sc Physics (Honours)
B.Sc Part-I
Paper-II

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Phase transition

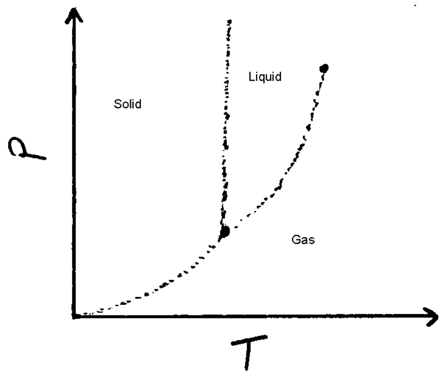
We are familiar with water, or carbon dioxide or alcohol changing from liquid to vapour, from solid to liquid, etc. We are aware that some metals are liquid at room temperature while most are solid and melt if the temperature is much higher. These are familiar phase changes.

More generally, a *phase transition* is a discontinuous change in the properties of a substance, not limited to changing physical structure from solid to liquid to gas, that takes place when PVT conditions are changed only slightly.

a. Phase diagram

Which phase of a substance is the stable phase depends on temperature and pressure. A *phase diagram* is a plot showing the conditions under which each phase is the stable phase.

For something like water or carbon dioxide, the phase diagram is divided into three regions—the solid, liquid, and gas (vapour) regions. If we trace the P,T values at which changes in phase take place, we trace the *phase boundaries* on the plot. At those particular values of P,T the two phases can coexist in equilibrium. At the *triple point*, all three phases coexist in equilibrium. The pressure on a gas-liquid or gas-solid boundary is called the *vapour pressure* of the liquid or solid.

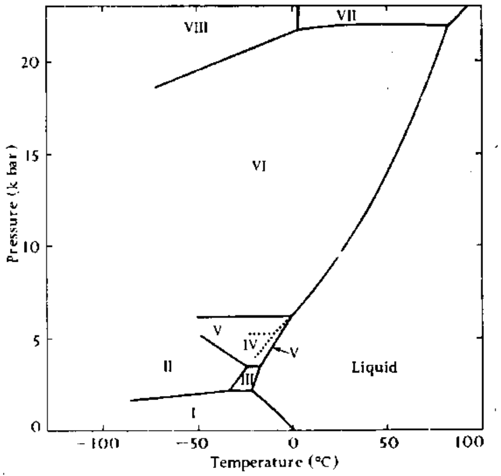


Notice that the phase boundary between gas and liquid has an end point, called the *critical point*. This signifies that at pressures and/or temperatures beyond the critical point there is no physical distinction between liquid and gas. The density of the gas is so great and the thermal motion of the liquid is so great that gas and liquid are the same.

Other sorts of phase transformations are possible, as for instance at very high pressures there are different solid phases of ice. Similarly for carbon, there is more than one solid phase—diamond and graphite. Diamond is the stable phase at very high pressure while graphite is the more stable phase at sea level air pressure. The glittery diamonds people pay so much to possess are ever so slowly changing into pencil lead.

Still other phase transformations are related not to pressure, but to magnetic field strength as in the case of ferromagnets and superconductors.

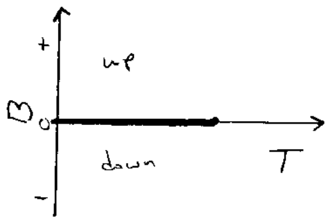
Here's a phase diagram for water, showing the several solid phases. They differ in crystal structure and density, as well as other properties such as electrical conductivity.



D. Eisenberg & W. Kauzmann, *The Structure and Properties of Water*, Oxford Univ. Press, 1969.

The phase diagram for water shown in the text figure 5.11 is a teensy strip along the T axis near $P = 0$ on this figure. [One bar is about one atmosphere of air pressure, so a kbar is 1000 atm.]

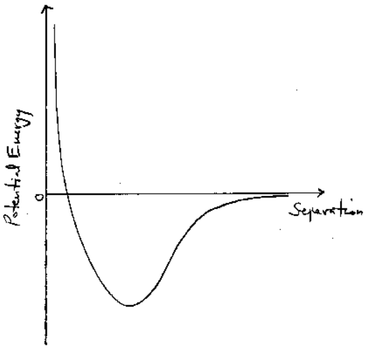
Here's a phase diagram for a ferromagnet, subjected to an external magnetic field, $\vec{B}$. The phase boundary is just the straight segment along the T axis. The segment ends at the critical point, at $T = T_c$.

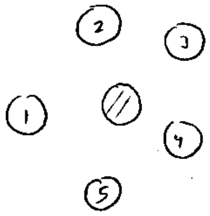


b. van der Waals model

There are phases because the particles interact with each other, in contrast to an ideal gas. The interactions are complicated (quantum mechanics), so we create simplified, effective models of the interparticle interactions in order to figure out what properties of the interactions lead to the observed phase diagrams. For instance, the van der Waals model: The model of a non-ideal gas is constructed as follows. Firstly, the atoms have nonzero volume—they are not really point particles. So, the volume of the system cannot go to zero, no matter how great the pressure or low the temperature. The smallest V can possibly be, let's say, is Nb. It's like shifting the origin from $V = 0$ to $V - Nb = 0$. Secondly, the atoms exert forces on each other. At short range, but not too short, the forces are attractive—the atoms tend to pull one another closer. This has the tendency to reduce the pressure that the system exerts outward on its environment (or container). We introduce a "correction" to the pressure that is proportional to the density $\left(\frac{N}{V}\right)$ and to the number of atoms in the system, N.

That is, $P \to P + \frac{\alpha N^2}{V^2}$.





With the new *V* and *P*, the gas law becomes the van der Waals equation of state:

$$\left(P+\frac{\alpha N^2}{V^2}\right)(V-Nb)=NkT \text{ or } P=\frac{NkT}{V-Nb}-\frac{\alpha N^2}{V^2}$$

Now, the *b* and α are adjustable parameters, whose values are different for different substances. They have to be fitted to empirical data.

There are countless other equations of state. For instance, there is the virial expansion, which is an infinite series,

$$PV=NkT\left(1+\frac{B(T)}{V}+\frac{C(T)}{V^2}+\cdots\right).$$

There is the Beattie-Bridgeman equation of state

$$PV=nkT+\frac{\beta}{V}+\frac{\gamma}{V^2}+\frac{\delta}{V^3}.$$

All represent "corrections" to the ideal gas equation of state.

c. Gibbs free energy—Clausius-Clapeyron—*PV* diagram

Which phase is stable at a given temperature and pressure is that phase with the lowest Gibbs free energy. On a phase boundary, where two phases coexist, there must be a common Gibbs free energy. That is, on the boundary between liquid and gas, $G_{liquid}=G_{gas}$. Imagine changing the pressure and temperature by small amounts in such a way as to remain on the phase boundary. Then the Gibbs free energy changes in such a way that

$$dG_{liquid}=dG_{gas}$$

$$-S_{liquid}dT+V_{liquid}dP+\mu_{liquid}dN=-S_{gas}dT+V_{gas}dP+\mu_{gas}dN$$

$$\frac{dP}{dT}=\frac{S_{gas}-S_{liquid}}{V_{gas}-V_{liquid}}$$

We've assumed that $dN = 0$. This result is the slope of the phase boundary curve on the *PT* diagram.

Commonly, we express the change in entropy in terms of the latent heat of the transformation, thusly

$$\frac{dP}{dT}=\frac{L}{T\Delta V}$$

This is the *Clausius-Clapeyron relation*, applicable to any *PT* phase boundary.

Finally, we compute the Gibbs free energy for the van der Waals model at a variety of temperatures and pressures to determine which phase is stable in each case.

$$dG = -SdT + VdP + \mu dN$$

Let $dN = 0$, and fix the temperature, varying only P.

$$dG = VdP$$

$$\begin{aligned}
\left(\frac{\partial G}{\partial V}\right)_{N,T} &= V\left(\frac{\partial P}{\partial V}\right)_{N,T} \\
&= V\left(\frac{\partial}{\partial V}\left(\frac{NkT}{V-Nb} - \frac{\alpha N^2}{V^2}\right)\right)_{N,T} \\
&= -\frac{NkTV}{(V-Nb)^2} + \frac{2\alpha N^2}{V^2} \\
&= -\frac{NkT(V-Nb)}{(V-Nb)^2} - \frac{NkT(Nb)}{(V-Nb)^2} + \frac{2\alpha N^2}{V^2}
\end{aligned}$$

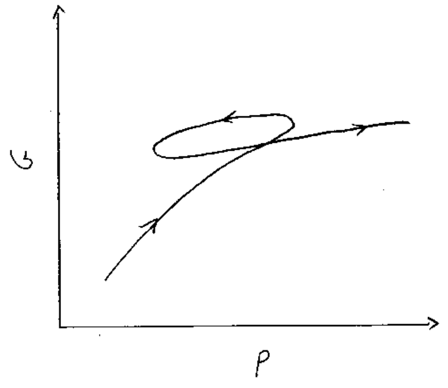
Integrate

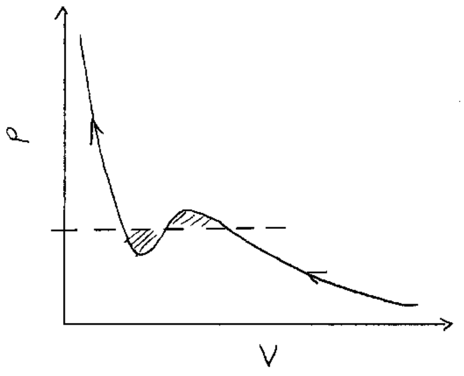
$$G = -NkT\ln(V-Nb) + \frac{(NkT)(Nb)}{V-Nb} - \frac{2\alpha N^2}{V} + c(T)$$

We have now expressions for both P and G as functions of V, at a fixed temperature, T. Firstly, we plot G vs. P at some fixed V. This yields a graph with a loop in it. The loop represents unstable states, since the Gibbs free energy is not a minimum. Integrating dG around the closed loop should give zero.

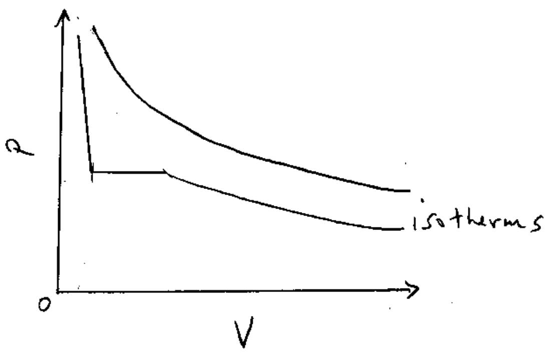
$$\oint dG = \oint \left(\frac{\partial G}{\partial P}\right)_T dP = \int VdP$$

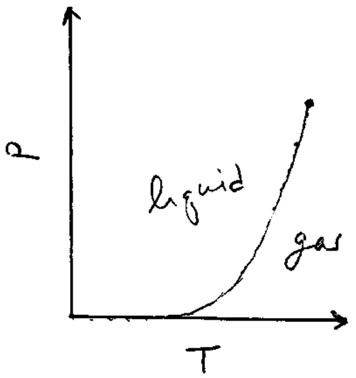
We plot out on a PV diagram the same points of free energy, and obtain an isotherm something like that shown on the diagram below right.





The pressure at which the phase transition occurs, at temperature T, is that value of P where the two shaded areas cancel. So, tracking along an isotherm from right to left, the gas is compressed and pressure rises until that horizontal section is reached. At that point, further compression does not increase the pressure because the gas is condensing to liquid. When the phase transition is complete, further compression causes a steep increase in pressure, with little decrease of volume, as the liquid is much less compressible than the gas. During the transition, both gas and liquid phases coexist.





If the temperature is high enough, there is no phase transition as *V* decreases. On a *PT* diagram, we see a phase boundary between the liquid and gas phases, up to the critical point, where the boundary terminates. Above the critical point, there is no distinction between gas and liquid. That would correspond to the isotherms having no flat segment on the *PV* diagram.

The van der Waals model is not very accurate in reality, but it does illustrate how the observed phase behavior arises from the interactions among the atoms or molecules of the substance.