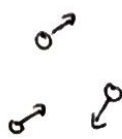




# Phase Changes

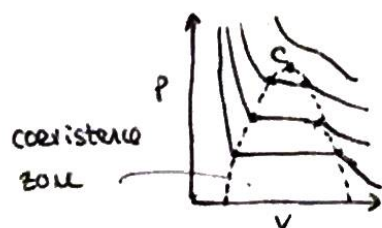
All the variables we have been talking about until now are also valid for solids and liquids, although the equations of state are different. The three states of matter are:

Gas:  Molecular spacing  $\gg$  size  
motion/position is random

Liquid:  spacing  $\approx$  size  
motion/position is random

Solid:  spacing = size  
motion/position is ordered

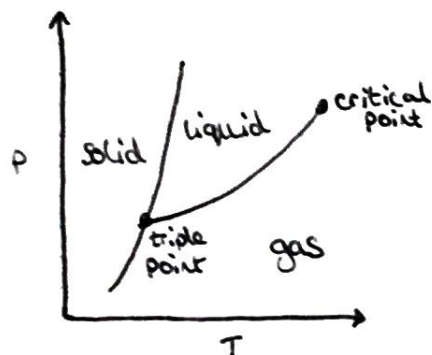
Consider a gas, cooling on an isotherm on a  $pV$  plot. Starting where the volume is large and the pressure is low and moving  $\leftarrow$ , the volume is decreasing, pressure is increasing and entropy is decreasing. On a microscopic level, this means increasing collision rates between molecules. At a certain point, condensation will occur. But the whole gas won't condense at once: once a certain fraction of the molecules are grouped in a "liquid phase", there will be enough room for the rest of the molecules to remain in gaseous form. This is called Coexistence. As the pressure continues to rise, more and more of the fluid will be in liquid form until there is no room for gas. At this point, the pressure starts to increase rapidly as liquids are harder to compress than gas.



Various isotherms are shown on the left. Point C is called the critical point. The region in the dotted lines is called the coexistence zone.

## Phase Diagrams

It might be easier to understand if we use a P-T diagram. A general diagram of a pure substance is shown below:



This might be a little confusing to look at to begin with. The curves are called coexistence curves and represent the pressure and temperature at which "neighbouring phases" can coexist in thermodynamic equilibrium.

The triple point is the singular point at which all three phases can coexist in thermodynamic equilibrium.

## The van der Waals' Model

This is a very simple model of real gas (not ideal) behaviour.

It starts with 2 assumptions:

- 1) Molecules occupy a non-zero volume
- 2) Molecules attract each other (due to van der Waals' forces)

This means we need to change our equations of state for ideal gases. We start by making:

$V \rightarrow V - n_m b$  and  $P \rightarrow P + \left(\frac{n_m}{V}\right)^2 a$  giving us:

$$\left(P + \left(\frac{n_m}{V}\right)^2 a\right)(V - n_m b) = n_m R T$$

where  $a$  represents the effect of the long range attraction of molecules and  $b$  represents the close-range repulsion of the molecules.

## Latent Heat

We can say, quite generally, that the gas phase is more disordered than the liquid phase which is more disordered than the solid phase:  $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

We can define a "specific entropy difference" between phases A and B as:

$$\Delta S_{AB} = \frac{S_B - S_A}{n_m}$$

We can work out the heat associated with this entropy change using  $dQ = TdS$ :

$Q = T \times n_m \times \Delta S_{AB}$ . We define  $L = \frac{Q}{n_m}$  as specific latent heat:

$$L = T \Delta S_{AB}$$

This is the specific latent heat associated with a phase change. In general,  $L$  takes a different value at different points on coexistence curves.

Trouton's Rule states that the specific latent heat of evaporation of many substances is well approximated by:

$$\underline{L \approx 10.5 R \times T_{\text{evaporation}}}$$

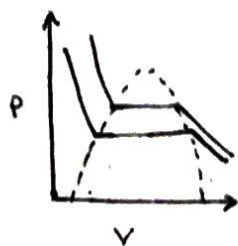
This is obtained from Boltzmann's definition of Entropy:

$\Delta S = N k_B \ln \left( \frac{V_{\text{gas}}}{V_{\text{liquid}}} \right)$  We can replace  $V_{\text{gas}}$  and  $V_{\text{liquid}}$  with the volume accessible for molecular motion. For a gas, we can ignore volume of molecules, and say it is just volume of the fluid. For a liquid, the "free volume" is found experimentally to generally be around 5% of the fluid volume. This gives  $\ln \left( \frac{V_g}{V_l} \right) \approx 10.5$ ,  $\therefore \underline{\underline{\Delta S \approx 10.5 R}}$



## Clausius-Clapeyron Relation

The coexistence curves on the  $P$ - $T$  diagram are described by the Clausius Clapeyron relation. To derive it, we need to look at two isotherms ( $T$  and  $T+dT$ ) on a  $P$ - $V$  diagram:



The path  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$  can be considered as a closed loop, giving  $\oint dU = 0$ .

$$\text{Therefore: } \oint P dV = \oint T dS$$

Since  $P$  and  $T$  are constant, this is pretty easy to calculate:  $\oint P dV = (P+dP)\Delta V - P\Delta V = dP\Delta V$

$$\oint T dS = (T+dT)\Delta S - T\Delta S = dT\Delta S$$

where  $\Delta V$  and  $\Delta S$  are the total change in volume and entropy from one phase to another. Thus, we get:

$$dP\Delta V = dT\Delta S \Rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad \text{but} \quad L = T\Delta S = \frac{T\Delta S}{\lambda_m}$$

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

This is the Clausius-Clapeyron relation.

It gives the gradient of the coexistence curves between all the phases.

We can apply this to, for example, the liquid-gas transition: we make the assumption that  $L$  is independent of temperature and the volume of the liquid is negligible compared to the volume of the gas:  $\Delta V \approx V_{\text{gas}}$

$$\therefore \frac{dP}{dT} = \frac{\lambda_m L}{TV_{\text{gas}}}$$

$$\text{but } PV = \lambda_m RT \Rightarrow \lambda_m = \frac{PV}{RT}$$

$$\frac{dP}{dT} = \frac{PL}{RT^2}$$

$$\therefore P(T) = P_0 \exp\left(-\frac{L}{RT}\right)$$

where  $P_0$  is the constant of integration.