

Phase transitions: real gases

Contents Phase diagrams of a simple substance - co-existence curves - Clausius - Clapeyron equation - discontinuous and continuous phase transitions - the van der Waals fluid - Maxwell construction and lever rule - unstable and metastable regions - critical exponents for a fluid.

We have already derived from statistical mechanics the thermodynamic properties of an ideal gas. Now, the isothermal compressibility of an ideal gas is easily shown to be $1/P$; hence, as one goes on increasing P , all that the gas becomes more and more difficult to compress further. In reality, however, as the molecules gets closer together the intermolecular attraction (usually called '*Van der Waals forces*') eventually causes a condensation of the gases into a liquid. An **ideal** gas doesn't take this attractive force into account, and hence it can't deal with the phenomenon of condensation. We must therefore turn to the study of **non-ideal** or **real** gases.

Before we do that (essentially in the framework of the Van der Waals equation of state), let us discuss briefly the phase diagram in the TP -plane of a typical 'simple' substance that can exist in the gas, liquid and solid (crystalline) phases, to gain an understanding of the broad qualitative features of the problem.

Note that all the figures that follow are schematic, meant for the purpose of illustration.

2.1 Phase diagram of a simple substance

Each point in the plane represents a thermodynamic equilibrium state of the substance. (For a given amount of the substance, the volume V is obtained from P and T via the equation of state appropriate to the phase concerned.) The lines represent co-existence curves: at a point on the 'boiling curve', for instance, the liquid and its vapour co-exist in thermal equilibrium. The boiling point of the liquid (or the condensation point of the vapour) is T_1 at a pressure P_1 ; the melting point of the solid (or the freezing point of the liquid) at T_2 at a pressure P_2 ; and so on.

The **triple point** is a very special point at which the three co-existence curves meet. At this point the solid, liquid and vapour can all co-exist. We have assumed for simplicity that the solid occurs in just a single crystalline structure.

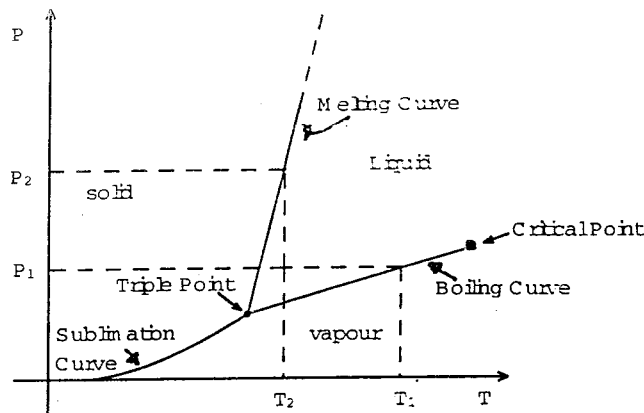
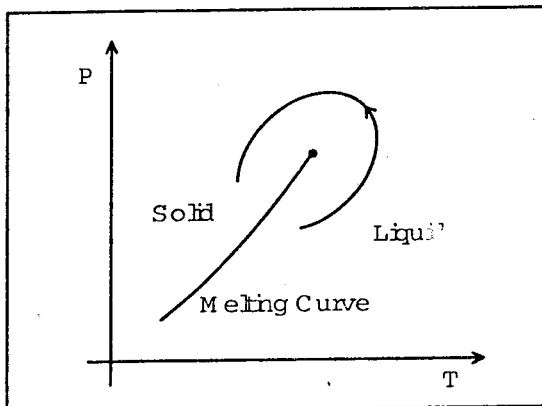


Figure 1: Phase diagram of a simple substance (not to scale)

In practice, more than one crystalline phases occurs, in general. Even so, one can show rigorously that for single-component systems, no more than three phases can co-exist in an equilibrium state. (Thus there can be no “quadruple point”, for instance.) We recall also that for H_2O , the triple point is at $T = 0.0075^\circ C$, $P = 4.58$ mm Hg.

The solid-vapour sublimation curve has been shown in the diagram to terminate on the T axis at its lower end. Zero pressure is of course not physical; what we mean to indicate is that even at low pressures, the system would tend to be in the ordered crystalline phase as $T \rightarrow 0K$, this being the state of lowest entropy. (S must vanish as $T \rightarrow 0$, in accord with the Nernst heat theorem.)

The solid-liquid melting curve extends upwards from the triple point. It has been depicted with a positive slope because for most substances an increase of the pressure increases the melting point. (Water is an exception. The melting curve has a negative slope in this case.) The curve keeps going indefinitely (unless it has a negative slope, in which case it would in principle terminate on the P -axis when $T = 0$ is reached). The melting curve cannot end abruptly at any point



Hypothetical coexistence line bet. solid & liquid. There can't be a critical point at its end (see text).

on the TP -plane (without encountering either a physical boundary such as the P -axis or another co-existence line). The reason for this is interesting. If the line did end abruptly at some point, one could take the system through a sequence of equilibrium points along a continuous path from the liquid state to the crystalline state, as shown in the figure alongside. But in the liquid state the atoms or the

molecules of the substance certainly don't exhibit the periodicity and ordering that they do in the crystalline state. In technical terms: the crystalline state has a certain **long-range order**; the liquid state doesn't. The crystal is invariant under a certain **discrete** group of translations and rotations called the crystallographic space group of the crystal; the liquid is homogeneous and isotropic, and so is invariant under arbitrary translations and rotations. There is no way in which one can go **continuously** from the homogeneity and isotropy of the liquid state to the discrete symmetry of the crystalline state. Hence the melting curve can't end abruptly in the TP plane. There is no 'critical point' at the tip of this curve as there is at the tip of the boiling curve, as can be seen in Fig. 1 (also see below).

The liquid-vapour boiling curve, on the other hand, can and does end abruptly at a point in the TP plane – the so-called critical point. Both liquids and gases are homogeneous and isotropic. Hence it is possible to go continuously via a sequence of equilibrium states from the vapour to the liquid state, and vice versa. Beyond the critical point, we have a merely a homogeneous, fluid phase: there is no distinction between the liquid and the vapour phases any longer. In fact, at the critical point, the meniscus demarcating the interface or boundary between the liquid and vapour phases disappears. (We shall comment further on the phase transitions from the liquid to the vapour state, or vice versa, shortly.) At any temperature above the critical temperature T_c , the substance can't be liquified by the application of pressure alone.

The slope of a co-existence curve

The reciprocal of a slope of a co-existence curve in the TP plane has a definite physical meaning; it tells us how the transition temperature (sublimation point, melting point or boiling point) varies with the pressure. The slope dP/dT is given by the Clausius-Clapeyron equation

$$\left(\frac{dP}{dT}\right) = \left(\frac{L}{T(v_2 - v_1)}\right). \quad (1)$$

We shall not go into the proof of this equation here, as it is treated in elementary thermodynamics. Here T is the transition temperature at the point concerned on the co-existence curve; L is the latent heat of transition; v_2, v_1 are the specific volumes of the two phases involved in the transition. Actually, this is a rather ambiguous way of writing the relation, as it doesn't tell us **which** of the two phases should be labelled phase 1, and which should be labelled phase 2. The 'correct' way of writing the equation is

$$\left(\frac{dP}{dT}\right) = \frac{(s_2 - s_1)}{(v_2 - v_1)}, \quad (2)$$

where s_1 and s_2 are the specific entropies in the two phases. In this form, it is evidently immaterial which of the two phases is labelled phase 1 and which is

labelled phase 2.

On the solid-liquid melting curve we may write

$$\left(\frac{dP}{dT}\right) = \frac{(s_{\text{liq}} - s_{\text{solid}})}{(v_{\text{liq}} - v_{\text{solid}})}. \quad (3)$$

As the numerator in the RHS is always positive (for normal liquids the liquid state is evidently more disordered than the crystalline one), the sign of the slope is determined by that of $(v_{\text{liq}} - v_{\text{solid}})$. If this is positive, as is usually the case, the melting temperature **increases** with increasing pressure. On the other hand, a substance like water freezes into a very 'open' crystalline structure, so that the density of the ice is lower than that of the water from which it freezes. Hence $(v_{\text{liq}} - v_{\text{solid}})$ is negative, and the melting temperature of ice **decreases** with increasing pressure. Moreover, the difference in entropy between solid and liquid is relatively large, while the change in volume is relatively small. The melting curve is therefore considerably **steeper** than the sublimation curve or the boiling curve.

On the liquid-vapour boiling curve, we may write

$$\left(\frac{dP}{dT}\right) = \frac{(s_{\text{vap}} - s_{\text{liq}})}{(v_{\text{vap}} - v_{\text{liq}})}. \quad (4)$$

Both the numerator and denominator on the RHS are positive. Hence dP/dT is always positive in this case. Moreover, the slope is generally quite small, owing to the fact that $(s_{\text{vap}} - s_{\text{liq}})$ is relatively small, and also – more significantly – the fact that $(v_{\text{vap}} - v_{\text{liq}})$ is generally relatively large.

Discontinuous phase transitions

The phase transitions across any of the co-existence curves is a **discontinuous** one, in contrast to the paramagnet-to-ferromagnet transition at the Curie temperature in zero applied magnetic field. It is very important to appreciate this difference.

In this case of the magnet, the spontaneous (or remnant) magnetization characterizes the phases, positive in the ferromagnetic 'up' phase, and negative in the ferromagnetic 'down' phase. Likewise, one way of characterizing the solid, liquid and vapour phases is via the specific volume (or density). [The matter is somewhat more intricate than this, especially when we want to distinguish between solid phases with different crystalline arrangements, but this simple approach will do for our present purposes.] The density changes **discontinuously** across a co-existence line – hence the terminology, 'discontinuous' phase transition. Such a transition is also called a **"first order" phase transition**; it can be shown that the **first derivative** of the free energy (with respect to a thermodynamic control

parameter such as T and P) is discontinuous at such a transition, although the free energy itself is continuous at that point.

In the magnet, too, we have a discontinuous phase transition from a ferromagnet 'up' state to a ferromagnet 'down' state, if we take the applied field across zero from positive to negative values or vice versa, at a temperature below the Curie point. We have already discussed magnetic phase transitions in simple terms. The spontaneous magnetization changes discontinuously from a positive value to minus this value as B crosses over from a positive to negative value. (See the figures below.) We shall return to the deep analogy between fluids and magnets shortly.

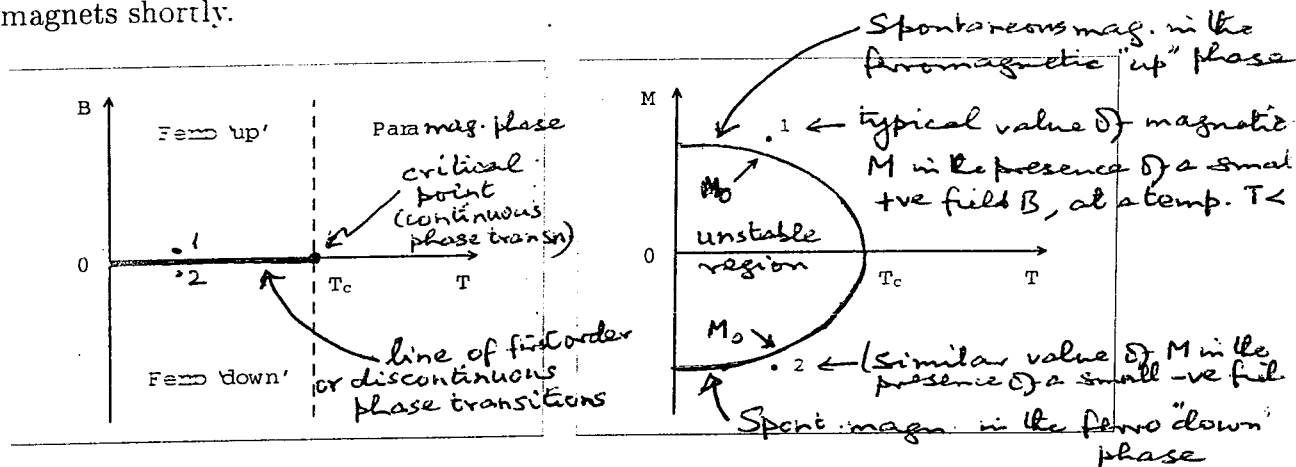


Figure 2: Phase diagrams for the simplest magnetic phase transitions

Continuous phase transitions

Exactly at the Curie temperature T_c , it is obvious that the jump in the spontaneous magnetization across the transition vanishes. We have also seen that the spontaneous magnetization takes off **continuously** from zero above T_c to a non-zero value below T_c as we cross T_c from $T > T_c$ to $T < T_c$ in zero applied field (see the figure on the right, above). Hence this is a **continuous** phase transition. Similarly, the line of first-order transitions represented by the boiling curve ends in a continuous transition at the critical point. The difference in specific volumes between the liquid and the vapour phases vanishes at this point. So does the latent heat of evaporation, or, equivalently, the difference in specific entropies between the liquid and vapour phases. We have already stated that the liquid-vapour interface (or meniscus) also disappears at this point, because the surface tension of the liquid also tends to zero at the critical point.

Continuous phase transitions are also called, in some cases, **second order phase transitions**. This is because in such cases the free energy and its first derivative are both continuous at the transition point, but the **second** derivative becomes discontinuous there. To take an example - in the para-to-ferromagnet

transition, we know that the magnetization remains continuous, but the susceptibility diverges. The former is the first derivative $[-(\partial F/\partial B)_T]_{B=0}$, while the latter is the second derivative $-(\partial^2 F/\partial B^2)_T]_{B=0}$. Similarly, at the critical point on the boiling curve, the difference in densities between the liquid and the vapour phases is zero (and it grows continuously as T is lowered from T_c), while the **compressibility** diverges at T_c - and the volume is $(\partial G/\partial P)_T$, while the (isothermal) compressibility is $-(1/V)(\partial^2 G/\partial P^2)_T$. However, the classification of phase transitions according to the order of the derivative of a free energy that becomes discontinuous is not of much practical use beyond the second order. This is because these higher derivatives are generally not directly or readily accessible to experiment.

It must be observed also that some of the transitions we have considered involve a breaking or decrease of symmetry, while others do not. The solid-to-liquid first order transition is a symmetry-breaking one, as is the second order para-to-ferromagnet transition at the Curie temperature. The liquid-to-gas transition does not involve any symmetry breaking; the ferromagnet "up" to ferromagnet "down" first order transition also does not involve any reduction in the symmetry of the thermodynamic state across the transition. When symmetry is broken or reduced, powerful arguments from the mathematics of group theory can be brought to bear on the problem to make very useful deductions of physical consequence. We do not go into this aspect here.

The Van der Waals gas

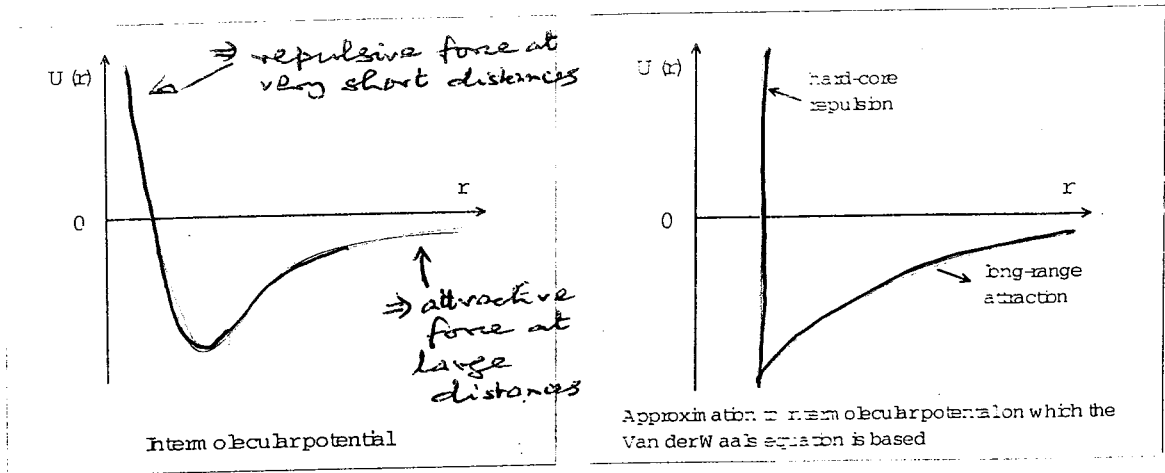
We have used a simple model equation of state in the case of magnetism to deduce several general results of a general nature. It is useful, similarly, to work with a model equation of state for a fluid to understand the liquid-vapour transition further. The simplest one in this context is the familiar Van der Waals equation of state, which we write for a gas of N particles as

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T. \quad (5)$$

This phenomenological equation simulates the effects of both a "hard core" repulsive interaction between the molecules of the gas at very small inter-particle distances, as well as a weak long-range attractive part that is responsible for condensation into a liquid as the pressure is increased (or as the temperature is lowered). The figure below shows the schematic variation of a typical inter-molecular potential with distance, as well as the approximation to this shape based on which the essential features of the Van der Waals equation of state can be derived in statistical mechanics. We do not go into this derivation here.

To run through some familiar results first: The Van der Waals (VdW) for

VB - Phase transitions



short) equation has a critical point given by the conditions

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad (6)$$

in addition to the equation itself. These three conditions uniquely determine the critical parameters. We find

$$T_c = 8a/(27k_B b), V_c = 3Nb, P_c = a/(27b^2). \quad (7)$$

The isotherms are shown in the figure that follows.

These isotherms are not drawn to scale. With realistic values of the parameters a and b , one gets curves in which the 'liquid' part of an isotherm (for $T < T_c$) is very steep, while the 'gas' or vapour part is rather flat. In a typical isotherm

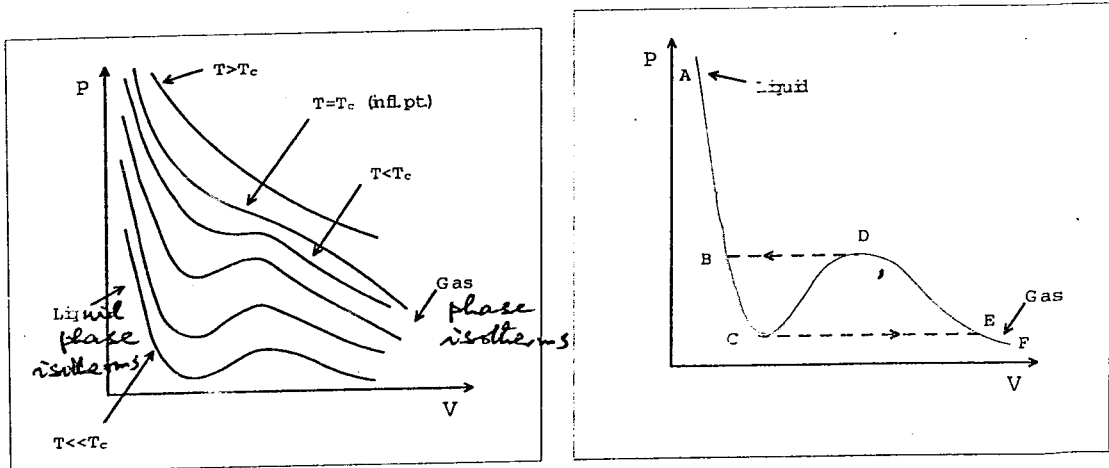


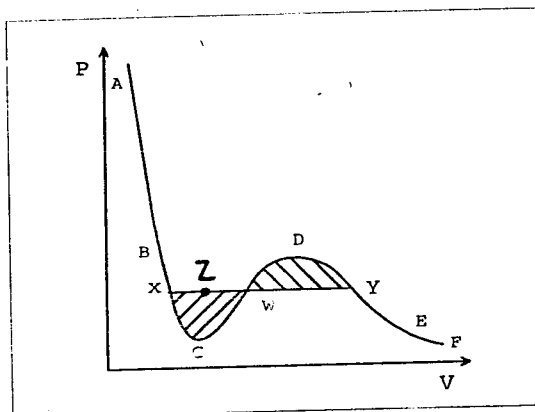
Figure 3: Isotherms

for $T < T_c$ (shown on the right), the portion CD is unphysical: the slope here is

positive, so that the compressibility of the system is negative, violating stability requirements (Le Chatelier's principle). This part is an artifact of the approximations involved in the VdW equation, and must therefore be discarded.

Even after this is done, the system would exhibit behaviour that is not observed in practice. If we begin with a vapour phase, say at F , and increase the pressure while staying on the isotherm, the system moves past E and reaches D . Thereafter, on a further increase of P , it has no recourse but to jump to B , and then continue upwards on the isotherm. Thus liquefaction occurs at the pressure P_D . On the other hand, if we start on the isotherm at A in the liquid state and decrease P , the system stays in the liquid state all the way down to C , and then jumps to the vapour state at E . Thus evaporation to the vapour state occurs on the return cycle at a different pressure, P_E . The fluid would thus exhibit hysteresis. But this is not observed, in general. The extremely rapid thermal fluctuations at a molecular level preclude hysteretic behaviour in a fluid, except under very carefully controlled conditions. Thus at least some portions of BC and ED are metastable - they represent respectively a superheated liquid and a supercooled vapour. These states are not stable thermodynamic equilibrium states. They can be realized under very carefully controlled experimental conditions using very pure samples, but they are easily perturbed, in which case they relapse into the appropriate equilibrium states.

We have said that some portions of BC and ED are metastable. The question is, at which point X (or Y) on the isotherm does the system make the transitions to the vapour state from the liquid state (or vice versa)?



The answer is provided by the so-called Maxwell or "tie-line" construction. The horizontal line XY , called the tie line, is placed such that the area between XW and the isotherm is equal to the area between WY and the isotherm. This equal-area rule can be shown to follow from the physical requirement that Gibbs free energies in the liquid and vapour states be equal at the co-existence point. [A rigorous demonstration of the validity of the rule starting from the basic principles of

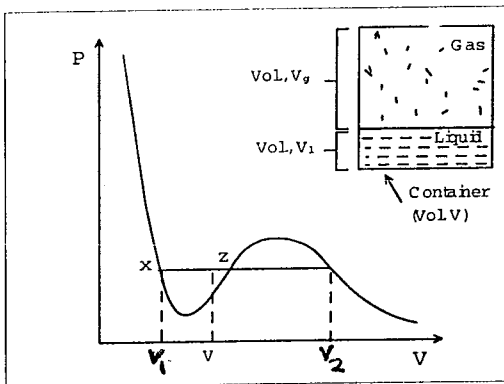
statistical mechanics is a research-level topic.]

Thus the 'true' isotherm corresponding to the VdW equation of state is of the form $ABXWYEF$, for $T < T_c$. The liquid-vapour transition occurs (for the temperature concerned) at the unique pressure $P_X (= P_Y)$. The volume of course changes discontinuously, from V_X to V_Y (or vice versa) - the transition is a discontinuous one, as we already know.

The lever rule

What happens if the system is suddenly placed at some point on the line XY , say at Z ? We know that at the pressure P_Z , the liquid and the vapour co-exist in thermal equilibrium. Hence the system will consist partly of a liquid phase, with vapour above it in the container. The **amounts** of each phase present are not arbitrary: they are given by the so-called **lever rule**:

Let M be the total mass of the substance, ρ_l the mass density in the liquid phase, and ρ_g the mass density in the gas phase. Let V_l and V_g be the respective volumes of the two phases in the container: $V_l + V_g = V$ while $\rho_l V_l + \rho_g V_g = M$. Hence



$$V_l = \frac{(M - \rho_g V)}{(\rho_l - \rho_g)},$$

$$V_g = \frac{(\rho_l V - M)}{(\rho_l - \rho_g)}.$$

Now, if the substance had been all liquid (at the same P and T), it would have occupied a volume V_1 . Therefore $\rho_l = M/V_1$. Similarly, if it had been entirely in the vapour phase, it would

have occupied a volume V_2 . Hence $\rho_g = M/V_2$. Putting these in, we obtain,

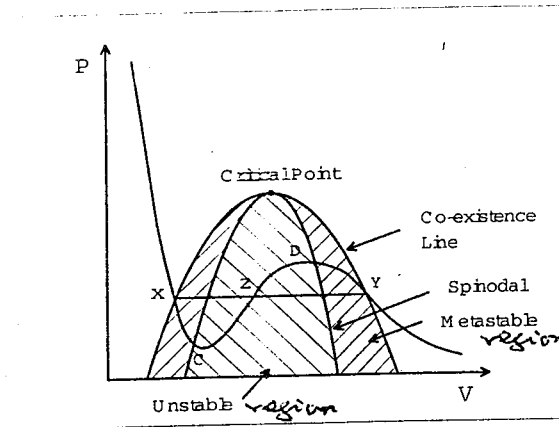
$$\frac{V_l}{V} = \frac{\left(\frac{1}{V} - \frac{1}{V_2}\right)}{\left(\frac{1}{V_1} - \frac{1}{V_2}\right)}, \quad \frac{V_g}{V} = \frac{\left(\frac{1}{V_1} - \frac{1}{V}\right)}{\left(\frac{1}{V_1} - \frac{1}{V_2}\right)} \quad (8)$$

Thus

$$\frac{\text{Mass of liquid portion at } Z}{\text{Mass of vapour portion at } Z} = \frac{\rho_l V_l}{\rho_g V_g} = \frac{(V_2 - V)}{(V - V_1)}. \quad (9)$$

An easy way to remember this is $\frac{M_{\text{liq}}}{M_{\text{vap}}} = \frac{YZ}{XZ}$, reminiscent of the "lever rule" for the moments of the forces operating in a lever.

The unstable and metastable regions

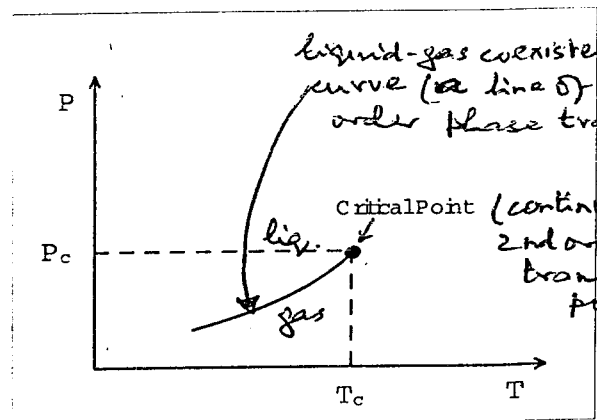
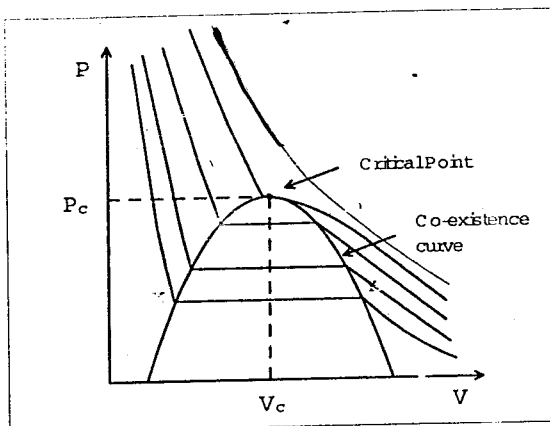


The locus of the points C, D and that of the points X, Y are shown alongside, with the appropriate labels. Note that the loci merge at the critical point. When the system is placed in the shaded region (stable or metastable), phase separation occurs; the system spontaneously separates into a part that is liquid and a part that is vapour. The relative amounts are given by the lever rule derived above.

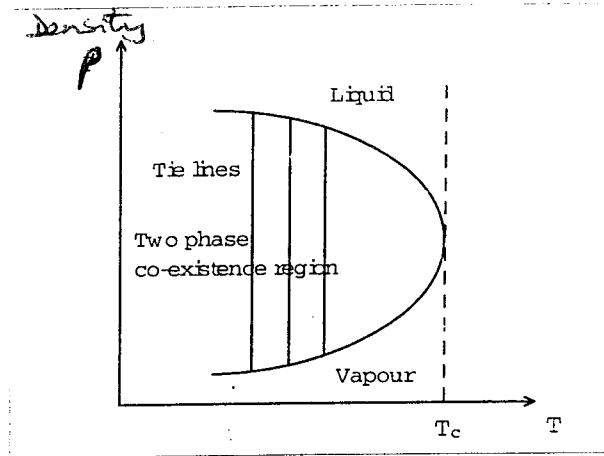
The locus of C, D separates the metastable region from the unstable region, and is called the *spinodal curve*. It is of importance in the study of solutions and mixtures in physical chemistry, metallurgy, etc.

The phase diagram for the liquid-vapour system

The PV and the PT diagrams have already been drawn in the foregoing. They are repeated here for ready reference. It remains to draw the VT diagram, the



analogue in the case of fluid of the MT diagram for a magnet. Equivalently, we could draw the variation of the density with the temperature. This is shown below, schematically. In practice, the variation of the density of the gas with temperature is much greater than that of the liquid. The curve is therefore not a symmetric parabola-like curve. But very close to the critical region, it is approximately parabolic, at least within the framework of the VdW model under discussion here.



The critical exponents for a fluid

Using the Van der Waals model, which is a mean field theory for a fluid, we may study the behaviour of the critical isotherm, the compressibility, the specific volume, etc. in the vicinity of the critical point. It is left as an exercise to show that the critical exponents β , γ and δ in the case of a fluid are exactly those found in our study of magnetism in mean field theory ($\beta = 1/2, \gamma = 1, \delta = 3$). This gives a deeper meaning to the fluid-magnet analogy, and is the starting point in the modern theory of phase transitions and critical phenomena.

$$\bullet \quad \kappa_T \equiv -\frac{1}{V} \frac{\partial V}{\partial P} \xrightarrow{T \rightarrow T_c} (T - T_c)^{-\gamma}$$

$$\bullet \quad \rho_{\text{liq}} - \rho_{\text{gas}} = \begin{cases} (T_c - T)^\beta & T < T_c \\ 0 & T > T_c \end{cases}$$

$$\bullet \quad \frac{P}{k_B T} \sim \text{const.} + c(P - P_c)^\delta$$