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Physical
Chemistry

UNDERSTANDING OUR CHEMICAL WORLD

5

Phase equilibria

Introduction

Phase equilibrium describes the way phases (such as solid, liquid and/or gas) co-exist at some temperatures and pressure, but interchange at others.

First, the criteria for phase equilibria are discussed in terms of single-component systems. Then, when the ground rules are in place, multi-component systems are discussed in terms of partition, distillation and mixing.

The chapter also outlines the criteria for equilibrium in terms of the Gibbs function and chemical potential, together with the criteria for spontaneity.

5.1 Energetic introduction to phase equilibria

Why does an ice cube melt in the mouth?

Introduction to phase equilibria

The temperature of the mouth is about $37\,°C$, so an overly simple explanation of why ice melts in the mouth is to say that the mouth is warmer than the transition temperature $T_{(melt)}$. And, being warmer, the mouth supplies energy to the immobilized water molecules, thereby allowing them to break free from those bonds that hold them rigid. In this process, solid H_2O turns to liquid H_2O – the ice melts.

Incidentally, this argument also explains why the mouth feels cold after the ice has melted, since the energy necessary to melt the ice comes entirely *from* the mouth. In consequence, the mouth has less energy after the melting than before; this statement is wholly in accord with the zeroth law of thermodynamics, since heat energy travels from the hot mouth to the cold ice. Furthermore, if the mouth is considered as an *adiabatic* chamber (see p. 89), then the only way for the energy to be found for melting is for the temperature of the mouth to fall.

Further thermodynamic background: terminology

In the thermodynamic sense, a *phase* is defined as part of a chemical system in which all the material has the same composition and state. Appropriately, the word comes from the Greek *phasis*, meaning 'appearance'. Ice, water and steam are the three simple phases of H_2O. Indeed, for almost all matter, the three simple phases are solid, liquid and gas, although we must note that there may be many different solid phases possible since $H_2O_{(s)}$ can adopt several different crystallographic forms. As a related example, the two stable phases of solid sulphur are its monoclinic and orthorhombic crystal forms.

> A *phase* is a component within a system, existing in a precisely defined physical state, e.g. gas, liquid, or a solid that has a single crystallographic form.

Ice is a solid form of water, and is its only stable form below $0\,^{\circ}C$. The liquid form of H_2O is the only stable form in the temperature range $0 < T < 100\,^{\circ}C$. Above $100\,^{\circ}C$, the normal, stable phase is gaseous water, 'steam'. Water's *normal* melting temperature $T_{(melt)}$ is $0\,^{\circ}C$ (273.15 K). The word 'normal' in this context implies 'at standard pressure $p^{\ominus}$'. The pressure $p^{\ominus}$ has a value of 10^5 Pa. This temperature $T_{(melt)}$ is often called the melting *point* because water and ice coexist indefinitely at this temperature and pressure, but at no other temperature can they coexist. We say they reside together at *equilibrium*.

> Concerning transitions between the two phases '1' and '2', Hess's Law states that $\Delta H_{(1\to2)} = -1 \times \Delta H_{(2\to1)}$.

To melt the ice, an amount of energy equal to $\Delta H^{\ominus}_{(melt)}$ must be added to overcome those forces that promote the water adopting a solid-state structure. Such forces will include hydrogen bonds. Re-cooling the melted water to re-solidify it back to ice involves the same amount of energy, but this time energy is *liberated*, so $\Delta H^{\ominus}_{(melt)} = -\Delta H^{\ominus}_{(freeze)}$. The freezing process is often called *fusion*. (Strictly, we ought to define the energy by saying that no pressure–volume work is performed during the melting and freezing processes, and that the melting and freezing processes occur without any changes in temperature.)

Table 5.1 gives a few everyday examples of phase changes, together with some useful vocabulary.

Two or more phases can coexist indefinitely provided that we maintain certain conditions of temperature T and pressure p. The normal boiling temperature of water is $100\,^{\circ}C$, because this is the only temperature (at $p = p^{\ominus}$) at which both liquid and

Table 5.1 Summary of terms used to describe phase changes

Phase transition	Name of transition	Everyday examples
Solid → gas	Sublimation	'Smoke' formed from dry ice
Solid → liquid	Melting	Melting of snow or ice
Liquid → gas	Boiling or vaporization	Steam formed by a kettle
Liquid → solid	Freezing, solidification or fusion	Ice cubes formed in a fridge; hail
Gas → liquid	Condensation or liquification	Formation of dew or rain
Gas → solid	Condensation	Formation of frost

gaseous H_2O coexist at *equilibrium*. Note that this equilibrium is *dynamic*, because as liquid is converted to gas an equal amount of gas is also converted back to liquid.

However, the values of pressure and temperature at equilibrium depend on each other; so, if we change the pressure, then the temperature of equilibrium shifts accordingly (as discussed further in Section 5.2). If we plotted all the experimental values of pressure and temperature at which equilibrium exists, to see the way they affect the equilibrium changes, then we obtain a graph called a *phase diagram*, which looks something like the schematic graph in Figure 5.1.

> A *phase diagram* is a graph showing values of applied pressure and temperature at which equilibrium exists.

We call each solid line in this graph a *phase boundary*. If the values of p and T lie on a phase boundary, then equilibrium between two phases is guaranteed. There are three common phase boundaries: liquid–solid, liquid–gas and solid–gas. The line separating the regions labelled 'solid' and 'liquid', for example, represents values of pressure and temperature at which these two phases coexist – a line sometimes called the 'melting-point phase boundary'.

> A *phase boundary* is a line on a phase diagram representing values of applied pressure and temperature at which equilibrium exists.

The point where the three lines join is called the *triple point*, because *three* phases coexist at this single value of p and T. The triple point for water occurs at $T = 273.16$ K (i.e. at $0.01\,°C$) and $p = 610$ Pa ($0.006p^{\ominus}$). We will discuss the *critical point* later.

Only a single phase is stable if the applied pressure and temperature do not lie on a phase boundary, i.e. in one of the areas *between* the phase boundaries. For example, common sense tells is that on a warm and sunny summer's day, and at normal pressure, the only stable phase of H_2O is liquid water. These conditions of p and T are indicated on the figure as point 'D'.

> The *triple point* on a phase diagram represents the value of pressure and temperature at which *three* phases coexist at equilibrium.
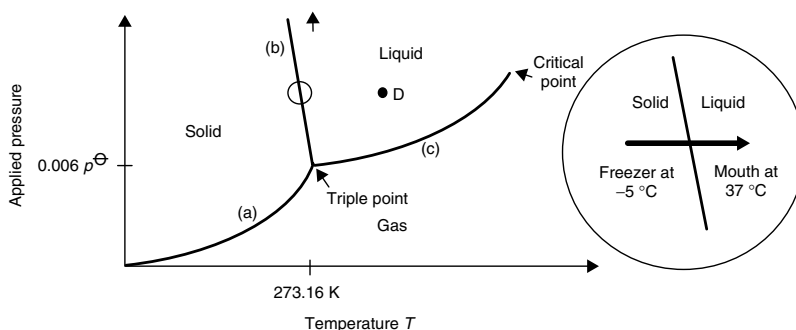

Figure 5.1   Schematic phase diagram showing pressures and temperatures at which two phases are at equilibrium. Phase boundary (a) represents the equilibrium between steam and ice; boundary (b) represents equilibrium between water and ice; and boundary (c) represents equilibrium between water and steam. The point **D** represents p and T on a warm, sunny day. *Inset*: warming an ice cube from $-5\,°C$ to the mouth at $37\,°C$ at constant pressure causes the stable phase to convert from solid to liquid. The phase change occurs at $0\,°C$ at $p^{\ominus}$

When labelling a phase diagram, recall how the only stable phase at high pressure and low temperature is a solid; a gas is most stable at low pressure and high temperature. The phase within the crook of the 'Y' is therefore a liquid.

We can predict whether an ice cube will melt just by looking carefully at the phase diagram. As an example, suppose we take an ice cube from a freezer at $-5\,^{\circ}$C and put it straightaway in our mouth at a temperature of $37\,^{\circ}$C (see the inset to Figure 5.1). The temperature of the ice cube is initially cooler than that of the mouth. The ice cube, therefore, will warm up as a consequence of the zeroth law of thermodynamics (see p. 8) until it reaches the temperature of the mouth. Only then will it attain equilibrium. But, as the temperature of the ice cube rises, it crosses the phase boundary, as represented by the bold horizontal arrow, and undergoes a *phase transition* from solid to liquid.

We know from Hess's law (see p. 98) that it is often useful to consider (mentally) a physical or chemical change by dissecting it into its component parts. Accordingly, we will consider the melting of the ice cube as comprising two processes: warming from $-5\,^{\circ}$C to $37\,^{\circ}$C, and subsequent melting at $37\,^{\circ}$C. During warming, the water crosses the phase boundary, implying that it changes from being a *stable* solid (when below $0\,^{\circ}$C) to being an *unstable* solid (above $0\,^{\circ}$C). Having reached the temperature of the mouth at $37\,^{\circ}$C, the solid ice converts to its stable phase (water) in order to regain stability, i.e. the ice cube melts in the mouth. (It would be more realistic to consider three processes: warming to $0\,^{\circ}$C, melting at constant temperature, then warming from 0 to $37\,^{\circ}$C.)

The Greek root *meta* means 'adjacent to' or 'near to'. Something *metastable* is almost stable ... but not quite.

Although the situation with melting in two stages appears a little artificial, we ought to remind ourselves that the phase diagram is made up of *thermodynamic* data alone. In other words, it is possible to see liquid water at $105\,^{\circ}$C, but it would be a *metastable* phase, i.e. it would not last long!

Aside

The arguments in this example are somewhat simplified.

Remember that the phase diagram's *y*-axis is the *applied* pressure. At room temperature and pressure, liquid water evaporates as a consequence of entropy (e.g. see p. 134). For this reason, both liquid and vapour are apparent even at s.t.p. The pressure of the vapour is known as the *saturated vapour pressure* (s.v.p.), and can be quite high.

The s.v.p. is not an applied pressure, so its magnitude is generally quite low. The s.v.p. of water will certainly be lower than atmospheric pressure. The s.v.p. increases with temperature until, at the boiling temperature, it equals the atmospheric pressure. One definition of boiling says that the s.v.p. equals the applied pressure.

The arguments in this section ignore the saturated vapour pressure.

Why does water placed in a freezer become ice?

Spontaneity of phase changes

It will be useful to concentrate on the diagram in Figure 5.2 when considering why a 'phase change' occurs *spontaneously*. We recall from Chapter 4 that one of the simplest tests of whether a thermodynamic event can occur is to ascertain whether the value of ΔG is negative (in which case the change is indeed spontaneous) or positive (when the change is not spontaneous).

The graph in Figure 5.2 shows the molar Gibbs function G_m as a function of temperature. (G_m decreases with temperature because of increasing entropy.) The value of G_m for ice follows the line on the left-hand side of the graph; the line in the centre of the graph gives values of G_m for liquid water; and the line on the right represents G_m for gaseous water, i.e. steam. We now consider the process of an ice cube being warmed from below $T_{(melt)}$ to above it. The molar Gibbs functions of water and ice become comparable when the temperature reaches $T_{(melt)}$. At $T_{(melt)}$ itself, the two values of G_m are the same – which is one definition of *equilibrium*. The two values diverge once more above $T_{(melt)}$.

Below $T_{(melt)}$, the two values of G_m are different, implying that the two forms of water are energetically different. It should be clear that if one energy is lower than the other, then the lower energy form is the stablest; in this case, the liquid water has a higher value of G_m and is less stable than solid ice (see the heavy vertical arrow, inset to Figure 5.2). Liquid water, therefore, is energetically unfavourable, and for that reason it is unstable. To attain stability, the liquid water must release energy and, in the process, undergo a phase change from liquid to solid, i.e. it freezes.

> Remember how the symbol Δ means 'final state minus initial state', so $\Delta G_m = G_{m\ (final\ state)} - G_{m\ (initial\ state)}$.
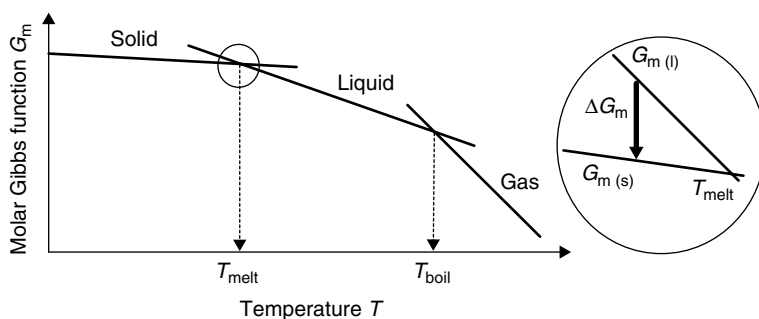

Figure 5.2 Graph of molar Gibbs function G_m as a function of temperature. *Inset*: at temperatures below $T_{(melt)}$ the phase transition from liquid to solid involves a negative change in Gibbs function, so it is spontaneous

These arguments represent a simple example of *phase equilibria*. This branch of thermodynamics tells us about the *direction* of change, but says nothing about the *rate* at which such changes occur.

It should be clear from the graph in Figure 5.2 that ΔG_m is negative (as required for a *spontaneous* change) only if the final state is *solid* ice and the initial state is *liquid* water. This sign of ΔG_m is all that is needed to explain why liquid water freezes at temperatures below $T_{(melt)}$.

Conversely, if an ice cube is warmed beyond $T_{(melt)}$ to the temperature of the mouth at $37\,^\circ$C, now it is the *solid* water that has excess energy; to stabilize it relative to liquid water at $37\,^\circ$C requires a different phase change to occur, this time *from* ice *to* liquid water. This argument again relies on the relative magnitudes of the molar Gibbs function, so ΔG_m is only negative at this higher temperature if the final state is liquid and the initial state is solid.

Why was Napoleon's Russian campaign such a disaster?

Solid-state phase transitions

A large number of French soldiers froze to death in the winter of 1812 within a matter of weeks of their emperor Napoleon Bonaparte leading them into Russia. The loss of manpower was one of the principal reasons why Napoleon withdrew from the outskirts of Moscow, and hence lost his Russian campaign.

But why was so ruthless a general and so obsessively careful a tactician as Napoleon foolhardy enough to lead an unprepared army into the frozen wastes of Russia? In fact, he thought he *was* prepared, and his troops were originally well clothed with thick winter coats. The only problem was that, so the story goes, he chose at the last moment to replace the brass of the soldiers' buttons with tin, to save money.

Metallic tin has many allotropic forms: rhombic white tin (also called β-tin) is stable at temperatures above $13\,^\circ$C, whereas the stable form at lower temperatures is cubic grey tin (also called α-tin). A transition such as tin$_{(white)} \rightarrow$ tin$_{(grey)}$ is called a *solid-state phase transition*.

Figure 5.3 shows the phase diagram of tin, and clearly shows the transition from tin$_{(white)}$ to tin$_{(grey)}$. Unfortunately, the tin allotropes have very different densities ρ, so $\rho_{(tin,\ grey)} = 5.8$ g cm^{-3} but $\rho_{(tin,\ white)} = 7.3$ g cm^{-3}. The difference in ρ during the transition from white to grey tin causes such an unbearable mechanical stress that the metal often cracks and turns to dust – a phenomenon sometimes called 'tin disease' or 'tin pest'.

The transition from white tin to grey was first noted in Europe during the Middle Ages, e.g. as the pipes of cathedral organs disintegrated, but the process was thought to be the work of the devil.
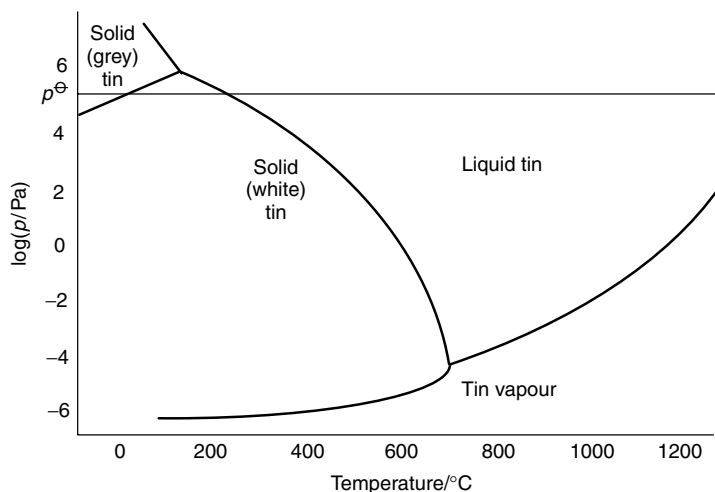
The air temperature when Napoleon entered Russia was apparently as low as $-35\,^\circ$C, so the soldiers' tin buttons converted from white to grey tin and, concurrently, disintegrated into powder. So, if this story is true, then Napoleon's troops froze to death because they lacked effective coat fastenings. Other common metals, such

Figure 5.3   Phase diagram of tin computed from thermodynamic data, showing the transition from grey tin from white tin at temperatures below 13 °C. Note the logarithmic *y*-axis. At $p^{\ominus}$, $T_{(white \rightarrow grey)} = 13$ °C, and $T_{(melt)} = 231.9$ °C. (Figure constructed from data published in *Tin and its Alloys and Compounds*, B. T. K. Barry and C. J. Thwaits, Ellis Horwood, Chichester, 1983)

as copper or zinc, and alloys such as brass, do not undergo phase changes of this sort, implying that the troops could have survived but for Napoleon's last-minute change of button material.

The kinetics of phase changes

Like all spontaneous changes, the rate at which the two forms of tin interconvert is a function of temperature. Napoleon's troops would have survived if they had entered Russia in the summer or autumn, when the air temperature is similar to the phase-transition temperature. The rate of conversion would have been slower in the autumn, even if the air temperature had been slightly less than $T_{(transition)}$ – after all, the tin coating of a can of beans does not disintegrate while sitting in a cool cupboard! The conversion is only rapid enough to noticeably destroy the integrity of the buttons when the air temperature is much lower than $T_{(transition)}$, i.e. when the difference between $T_{(air)}$ and $T_{(transition)}$ is large.

   Phase changes involving liquids and gases are generally fast, owing to the high mobility of the molecules. Conversely, while phase changes such as $tin_{(white)} \rightarrow tin_{(grey)}$ can and do occur in the solid state, the reaction is usually very much slower because it must occur wholly in the solid state, often causing any thermodynamic instabilities to remain 'locked in'; as an example, it is clear from the phase diagram of carbon in Figure 5.4 that graphite is the stable form of carbon (cf. p. 109), yet the phase change $carbon_{(diamond)} \rightarrow carbon_{(graphite)}$ is so slow that a significant extent of conversion requires millions of years.

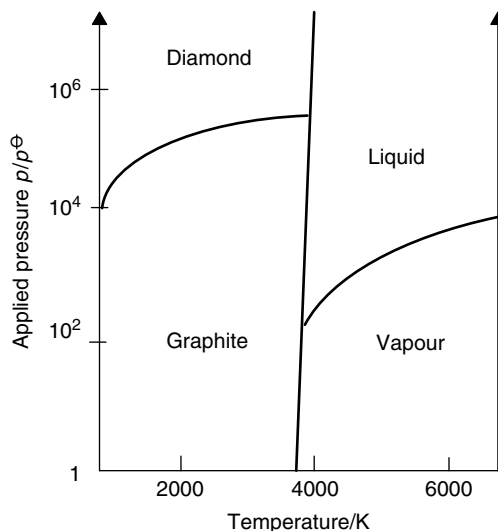   We consider chemical kinetics further in Chapter 8.

Figure 5.4 The phase diagram of carbon showing the two solid-state extremes of diamond and graphite. Graphite is the thermodynamically stable form of carbon at room temperature and pressure, but the rate of the transition $C_{(diamond)} \rightarrow C_{(graphite)}$ is virtually infinitesimal

5.2 Pressure and temperature changes with a single-component system: qualitative discussion

How is the 'Smoke' in horror films made?

Effect of temperature on a phase change: sublimation

Horror films commonly show scenes depicting smoke or fog billowing about the screen during the 'spooky' bits. Similarly, smoke is also popular during pop concerts, perhaps to distract the fans from something occurring on or off stage. In both cases, it is the adding of dry ice to water that produces the 'smoke'.

Dry ice is solid carbon dioxide.

Dry ice is carbon dioxide (CO_2) in its solid phase. We call it 'dry' because it is wholly liquid-free at $p^{\ominus}$: such solid CO_2 looks similar to normal ice (solid water), but it 'melts' without leaving a puddle. We say it *sublimes*, i.e. undergoes a phase change involving direct conversion from solid to gas, without liquid forming as an intermediate phase. $CO_{2(l)}$ can only be formed at extreme pressures.

Solid CO_2 is slightly denser than water, so it sinks when placed in a bucket of water. The water is likely to have a temperature of $20\,°C$ or so at room temperature, while typically the dry ice has a maximum temperature of ca $-78\,°C$ (195 K). The stable phase at the temperature of the water is therefore gaseous CO_2. We should understand that the $CO_{2(s)}$ is thermodynamically unstable, causing the phase transition $CO_{2(s)} \rightarrow CO_{2(g)}$ on immersion in the water.
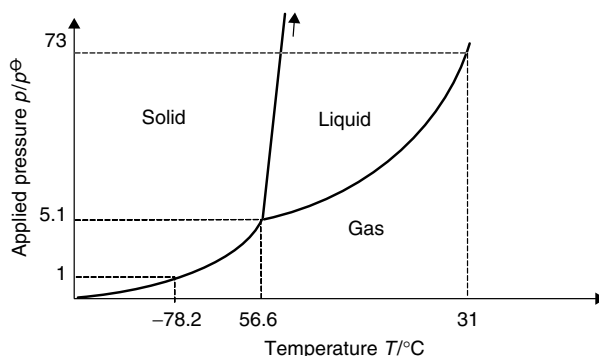
Figure 5.5   Phase diagram of a system that sublimes at room temperature: phase diagram of carbon dioxide. (Note that the y-axis here is logarithmic)

Incidentally, the water in the bucket is essential for generating the effect of theatrical 'smoke' because the large volumes of $CO_{2(g)}$ entrap minute particles of water (which forms a *colloid*; see Chapter 10.2). This colloidal water is visible because it creates the same atmospheric condition known as *fog*, which is opaque.

Look at the phase diagram of CO_2 in Figure 5.5, which is clearly similar in general form to the schematic phase diagram in Figure 5.1. A closer inspection shows that some features are different. Firstly, notice that the phase boundary between solid and liquid now has a positive gradient; in fact, water is almost unique in having a negative gradient for this line (see Section 5.1). Secondly, the conditions of room temperature ($T = 298$ K and $p = p^{\ominus}$) relate to conditions of the solid–gas phase boundary rather than the liquid–gas phase boundary.

By drawing a horizontal line across the figure at $p = p^{\ominus}$, we see how the line cuts the solid–gas phase boundary at $-78.2\,°C$. Below this temperature, the stable form of CO_2 is solid dry ice, and $CO_{2(g)}$ is the stable form above it. Liquid CO_2 is never the stable form at $p^{\ominus}$; in fact, Figure 5.5 shows that $CO_{2(l)}$ will not form at pressures below $5.1 \times p^{\ominus}$. In other words, liquid CO_2 is *never* seen naturally on Earth; which explains why dry ice sublimes rather than melts under s.t.p. conditions.

How does freeze-drying work?

Effect of pressure change on a phase change

Packets of instant coffee proudly proclaim that the product has been 'freeze-dried'. In practice, beans of coffee are ground, boiled in water and filtered to remove the depleted grounds. This process yields conventional 'fresh' coffee, as characterized by its usual colour and attractive smell. Finally, water is removed from the coffee solution to prepare granules of 'instant' coffee.

In principle, we could remove the water from the coffee by just boiling it off, to leave a solid residue as a form of 'instant coffee'. In fact, some early varieties of instant coffee were made in just this way, but the flavour was generally unpleasant as

How is coffee decaffeinated?

Critical and supercritical fluids

We continue our theme of 'coffee'. Most coffees contain a large amount of the heterocyclic stimulant *caffeine* (**I**). Some people prefer to decrease the amounts of caffeine they ingest for health reasons, or they simply do not like to consume it at all, and they ask for *decaffeinated* coffee instead.

(I)
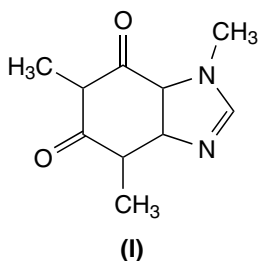
The modern method of removing **I** from coffee resembles the operation of a coffee percolator, in which the water-soluble chemicals giving flavour, colour and aroma are leached from the ground-up coffee during constant irrigation with a stream of boiling water.

Figure 5.8 shows such a system: we call it a *Soxhlet* apparatus. Solvent is passed continually through a porous cup holding the ground coffee. The solvent removes the caffeine and trickles through the holes at the bottom of the cup, i.e. as a solution of caffeine. The solvent is then recycled: solvent at the bottom of the flask evaporates to form a gas, which condenses at the top of the column. This pure, clean solvent then irrigates the coffee a second time, and a third time, etc., until all the caffeine has been removed.

Water is a good choice of solvent in a standard kitchen percolator because it removes all the water-soluble components from the coffee – hence the flavour. Clearly, however, a different solvent is required if only the caffeine is to be removed. Such a solvent must be cheap, have a low boiling point to prevent charring of the coffee and, most importantly, should leave no toxic residues. The presence of any residue would be unsatisfactory to a customer, since it would almost certainly leave a taste; and there are also health and safety implications when residues persist.

The preferred solvent is *supercritical* CO_2. The reasons for this choice are many and various. Firstly, the CO_2 is not hot (CO_2 first becomes critical at 31 °C and 73 atm pressure; see Figure 5.5), so no charring of the coffee occurs during decaffeination. Furthermore, at such a low temperature, all the components within the coffee that impart the flavour and aroma remain within the solid coffee – try soaking coffee beans in cold water and see how the water tastes afterwards! Caffeine is removed while retaining a full flavour.

> CO_2 is *super*critical at temperatures and pressures *above* the critical point.
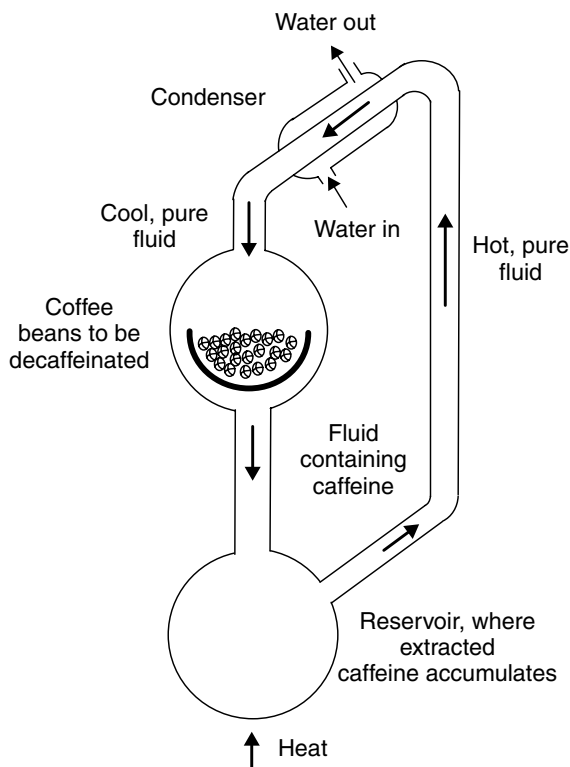
Figure 5.8 Coffee is decaffeinated by constantly irrigating the ground beans with supercritical carbon dioxide: schematic representation of a Soxhlet apparatus for removing caffeine from coffee

Secondly, solid CO_2 is relatively cheap. Finally, after caffeine removal, any occluded CO_2 will vaporize from the coffee without the need to heat it or employ expensive vacuum technology. Again, we retain the volatile essential oils of the coffee. Even if some CO_2 were to persist within the coffee granules, it is chemically inert, has no taste and would be released rapidly as soon as boiling water was added to the solid, decaffeinated coffee.

What is a critical or supercritical fluid?

We look once more at the phase diagram of CO_2 in Figure 5.5. The simplest way of obtaining the data needed to construct such a figure would be to take a sample of CO_2 and determine those temperatures and pressures at which the liquid, solid and gaseous phases coexist *at equilibrium*. (An appropriate apparatus involves a robust container having an observation window to allow us to observe the meniscus.) We then plot these values of p (as 'y') against T (as 'x').

We first looked at critical fluids on p. 50.

Let us consider more closely what happens as the conditions become more extreme inside the observation can. As heating proceeds, so the amount of $CO_{2(l)}$ converting to form gas increases. Accordingly, the amount of CO_2 within the gaseous phase increases, which will cause the density ρ of the vapour to increase. Conversely, if we consider the liquid, at no time does its *density* alter appreciably, even though its volume decreases as a result of liquid forming vapour.

From a consideration of the relative densities, we expect the liquid phase to reside at the bottom of the container, with the less-dense gaseous phase 'floating' above it. The 'critical' point is reached when the density of the gas has increased until it becomes the *same* as that of the liquid. In consequence, there is now no longer a lighter and a heavier phase, because $\rho_{(liquid)} = \rho_{(vapour)}$. Accordingly, we no longer see a meniscus separating liquid at the bottom of the container and vapour above it: it is impossible to see a clear distinction between the liquid and gas components. We say that the CO_2 is *critical*.

Further heating or additional increases in pressure generate *supercritical* CO_2. The pressure and temperature at which the fluid first becomes critical are respectively termed $T_{(critical)}$ and $p_{(critical)}$. Table 5.2 contains a few examples of $T_{(critical)}$ and $p_{(critical)}$.

The inability to distinguish liquid from gaseous CO_2 explains why we describe critical and supercritical systems as *fluids* – they are neither liquid nor gas.

It is impossible to distinguish between the liquid and gaseous phases of CO_2 at and above the critical point, which explains why a phase diagram has no phase boundary at temperatures and pressures above $T_{(critical)}$. The formation of a critical fluid has an unusual corollary: at temperatures above $T_{(critical)}$, we cannot cause the liquid and gaseous phases to separate by decreasing or increasing the pressure alone. The critical temperature, therefore, represents the maximum values of p and T at which liquification

> It is impossible to distinguish between the liquid and gaseous phases of CO_2 at temperatures and pressures at and above the critical point.

> The intensive properties of the liquid and gas (density, heat capacity, etc.) become equal at the *critical point*, which is the highest temperature and pressure at which both the liquid and gaseous phases of a given compound can coexist.

> IUPAC defines *supercritical chromatography* as a separation technique in which the mobile phase is kept above (or relatively close to) its critical temperature and pressure.

Table 5.2 Critical constants $T_{(critical)}$ and $p_{(critical)}$ for some common elements and bi-element compounds

Substance	$T_{(critical)}/K$	$p_{(critical)}/p^{\ominus}$
H_2	33.2	12.97
He	5.3	2.29
O_2	154.3	50.4
Cl_2	417	77.1
CO_2	304.16	73.9
SO_2	430	78.7
H_2O	647.1	220.6
NH_3	405.5	113.0

of the gas is possible. We say that there cannot be any $CO_{2(l)}$ at temperatures above $T_{(critical)}$.

Furthermore, supercritical CO_2 does not behave as merely a *mixture* of liquid and gaseous CO_2, but often exhibits an exceptional ability to solvate molecules in a specific way. The removal of caffeine from coffee relies on the chromatographic separation of caffeine and the other organic substances in a coffee bean; supercritical fluid chromatography is a growing and exciting branch of chemistry.

5.3 Quantitative effects of pressure and temperature change for a single-component system

Why is ice so slippery?

Effect of p and T on the position of a solid–liquid equilibrium

> The coefficient of friction μ (also called 'friction factor') is the quotient of the frictional force and the normal force. In other words, when we apply a force, is there a resistance to movement or not?

We say something is 'as slippery as an ice rink' if it is has a tiny coefficient of friction, and we cannot get a grip underfoot. This is odd because the coefficient of friction μ for ice is quite high – try dragging a fingernail along the surface of some ice fresh from the ice box. It requires quite a lot of effort (and hence work) for a body to move over the surface of ice.

At first sight, these facts appear to represent a contradiction in terms. In fact, the reason why it is so easy to slip on ice is that ice usually has a thin layer of liquid water covering its surface: it is this water–ice combination that is treacherous and slippery.

But why does any water form on the ice if the weather is sufficiently cold for water to have frozen to form ice? Consider the ice directly beneath the blade on a skater's ice-shoe in Figure 5.9: the edge of the blade is so sharp that an enormous pressure is exerted on the ice, as indicated by the grey tints.

> The sign of dp/dT for the liquid–solid line on a phase diagram is almost always positive. Water is the only common exception.

We now look at the phase diagram for water in Figure 5.10. Ice melts at $0\,°C$ if the pressure is $p^{\ominus}$ (as represented by T_1 and p_1 respectively on the figure). If the pressure exerted on the ice increases to p_2, then the freezing temperature decreases to T_2. (The freezing temperature *decreases* in response to the *negative* slope of the liquid–solid phase boundary (see the inset to Figure 5.10), which is most unusual; virtually all other substances show a positive slope of dp/dT.)

If the temperature T_2 is lower than the freezing temperature of the water – and it usually is – then some of the ice converts to form liquid water; squeezing decreases the freezing temperature of the water. The water-on-ice beneath the skater's blade is slippery enough to allow effortless skating.
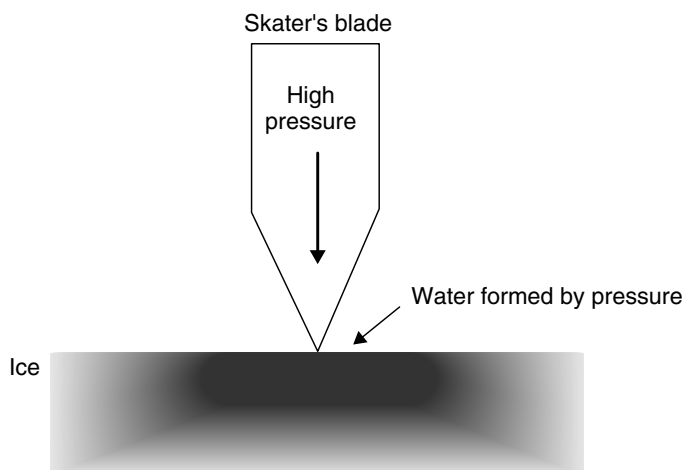
Figure 5.9   Skaters apply an enormous pressure beneath the blades of their skates. This pressure causes solid ice to melt and form liquid water
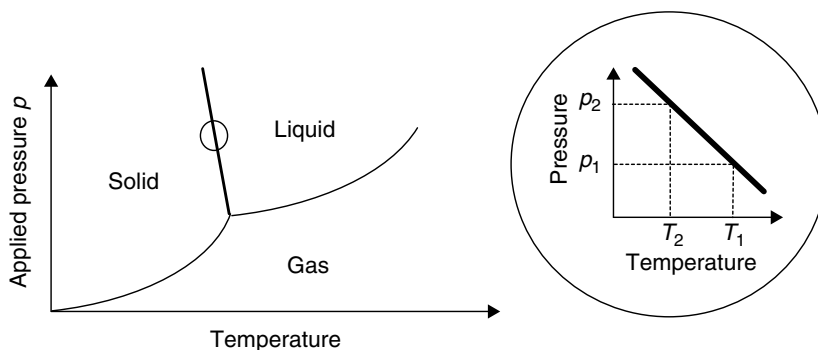

Figure 5.10   Phase diagram of water. *Inset*: applying a high pressure from p_1 (here $p^{\ominus}$) to p_2 causes the melting temperature of the ice to decrease from temperature T_1 (here $0\,^{\circ}C$) to T_2

What is 'black ice'?

The Clapeyron equation

We give the name 'black ice' to the phenomenon of invisible ice on a road. In practice, anything applying a pressure to solid ice will cause a similar depression of the freezing temperature to that of the skater, so a car or heavy vehicle travelling over ice will also cause a momentary melting of the ice beneath its wheels. This water-on-ice causes the car to skid – often uncontrollably – and leads to many deaths every year. Such ice is particularly dangerous: whereas an ice skater wants the ice to be slippery, a driver does not.

Aside

If water behaved in a similar fashion to most other materials and possessed a *positive* value of ΔV_m, then water would spontaneously freeze when pressure was applied, rather than solid ice melting under pressure. Furthermore, a positive value of ΔV_m would instantly remove the problems discussed above, caused by vehicles travelling over 'black' ice, because the ice would remain solid under pressure; and remember that the slipperiness occurs because liquid water forms on top of solid ice.

Unfortunately, a different problem would present itself if ΔV_m was positive! If ΔV_m was positive, then Equation (5.1) shows that applying a pressure to liquid water would convert it to ice, even at temperatures slightly higher than $0\,^\circ\text{C}$, which provides a *different* source of black ice.

Why does a pressure cooker work?

The Clausius–Clapeyron equation

A pressure cooker is a sealed saucepan in which food cooks faster than it does in a simple saucepan – where 'simple', in this context means a saucepan that is open to the air. A pressure cooker is heated on top of a cooker or hob in the conventional way but, as the water inside it boils, the formation of steam rapidly causes the internal pressure to increase within its sealed cavity; see Figure 5.11. The internal pressure inside a good-quality pressure cooker can be as high 6 atm.

The phase diagram in Figure 5.12 highlights the pressure–temperature behaviour of the boiling (gas–liquid) equilibrium. The *normal* boiling temperature $T_{(boil)}$ of water is $100\,^\circ\text{C}$, but $T_{(boil)}$ increases at higher pressures and decreases if the pressure de-

> Remember that all equilibria are *dynamic*.

creases. As a simple example, a glass of water would boil instantly at the cold temperature of 3 K in the hard vacuum of deep space. The inset to Figure 5.12
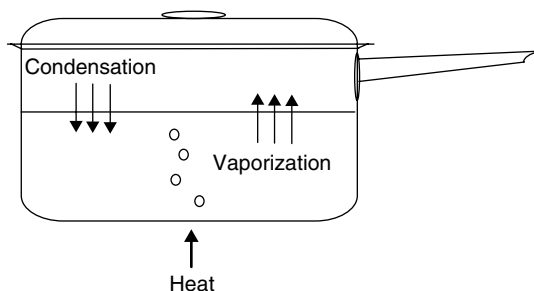

Figure 5.11 A pressure cooker enables food to cook fast because its internal pressure is high, which elevates the temperature at which food cooks
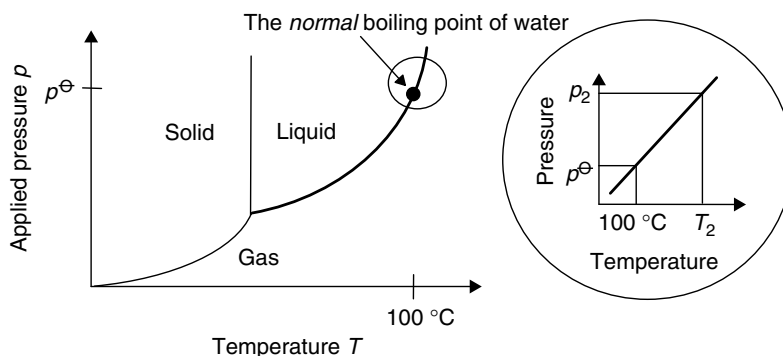
Figure 5.12 Phase diagram to show how a pressure cooker works. *Inset*: applying a high pressure from $p^{\ominus}$ to p_2 causes the boiling temperature of the water to increase from temperature $100\,^{\circ}\text{C}$ to T_2

shows why the water inside the pressure cooker boils at a higher temperature as a consequence of the pan's large internal pressure.

The *Clausius–Clapeyron equation* quantifies the way a boiling temperature changes as a function of the applied pressure. At the boiling points of T_1 and T_2, the external pressures p_1 and p_2 are the same as the respective vapour pressures.

Having qualitatively discussed the way a pressure cooker facilitates rapid cooking, we now turn to a quantitative discussion. The Clapeyron equation, Equation (5.1), would lead us to suppose that $\mathrm{d}p \propto \mathrm{d}T$, but the liquid–gas phase boundary in Figure 5.12 is clearly curved, implying deviations from the equation. Therefore, we require a new version of the Clapeyron equation, adapted to cope with the large volume change of a gas. To this end, we introduce the *Clausius–Clapeyron equation*:

$$\ln\left(\frac{p_2 \text{ at } T_2}{p_1 \text{ at } T_1}\right) = -\frac{\Delta H_{(\text{boil})}^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (5.5)$$

where R is the familiar gas constant, and $\Delta H_{(\text{boil})}^{\ominus}$ is the *enthalpy of vaporization*. $\Delta H_{(\text{boil})}^{\ominus}$ is always *positive* because energy must be put *in* to a liquid if it is to boil. T_2 here is the boiling temperature when the applied pressure is p_2, whereas changing the pressure to p_1 will cause the liquid to boil at a different temperature, T_1.

It does not matter which of the values we choose as '1' and '2' provided that T_1 relates to p_1 and T_2 relates to p_2. It is permissible to swap T_1 for T_2 and p_1 for p_2 simultaneously, which amounts to multiplying both sides of the equation by '−1'.

We need to understand that the Clausius–Clapeyron equation is really just a special case of the Clapeyron equation, and relates to phase changes in which *one of the phases is a gas*.

Worked Example 5.2 What is the boiling temperature of pure water inside a pressure cooker? Let T_1 be the normal boiling temperature $T_{(\text{boil})}$ of water (i.e. $100\,^{\circ}\text{C}$, 373 K, at $p^{\ominus}$) and let p_2 of $6 \times p^{\ominus}$ be the pressure inside the pan. The enthalpy of boiling water is 50.0 kJ mol^{-1}.

In this example, it is simpler to insert values into Equation (5.5) and to rearrange later. Inserting values gives

$$\ln\left(\frac{6 \times p^{\ominus}}{p^{\ominus}}\right) = \frac{-50\,000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{mol}^{-1}} \times \left(\frac{1}{T_2} - \frac{1}{373 \text{ K}}\right)$$

> Notice how the *ratio* within the bracket on the left-hand side of the Clausius–Clapeyron equation permits us to dispense with *absolute* pressures.

We can omit the units of the two pressures on the left-hand side because Equation (5.5) is written as a ratio, so the units cancel: we require only a *relative* change in pressure.

$$\ln 6.0 = -6104 \text{ K} \times \left(\frac{1}{T_2} - \frac{1}{373 \text{ K}}\right)$$

where ln 6.0 has a value of -1.79. Next, we rearrange slightly by dividing both sides by 6104 K, to yield:

$$\frac{-1.79}{6104 \text{ K}} = \frac{1}{T_2} - \frac{1}{373 \text{ K}}$$

so

$$\frac{1}{T_2} = -2.98 \times 10^{-4} \text{ K}^{-1} + \frac{1}{373 \text{ K}}$$

and

$$\frac{1}{T_2} = 2.38 \times 10^{-3} \text{ K}^{-1}$$

We obtain the temperature at which water boils by taking the reciprocal of both side. T_2, is 420 K, or 147 °C at a pressure of $6 \times p^{\ominus}$, which is much higher than the normal boiling temperature of 100 °C.

SAQ 5.4 A mountaineer climbs Mount Everest and wishes to make a strong cup of tea. He boils his kettle, but the final drink tastes lousy because the water boiled at too low a temperature, itself because the pressure at the top of the mountain is only $0.4 \times p^{\ominus}$. Again taking the enthalpy of boiling the water to be 50 kJ mol^{-1} and the normal boiling temperature of water to be 373 K, calculate the temperature of the water as it boils at the top of the mountain.

The form of the Clausius–Clapeyron equation in Equation (5.5) is called the *integrated* form. If pressures are known for more than two temperatures, an alternative form may be employed:

$$\ln p = -\frac{\Delta H^{\ominus}_{(\text{boil})}}{R} \times \frac{1}{T} + \text{constant} \tag{5.6}$$

so a graph of the form '$y = mx + c$' is obtained by plotting ln p (as 'y') against $1/T$ (as 'x'). The gradient of this *Clapeyron graph* is '$-\Delta H^{\ominus}_{(boil)} \div R$', so we obtain $\Delta H^{\ominus}_{(boil)}$ as 'gradient $\times -1 \times R$'.

> We employ the *integrated* form of the Clausius–Clapeyron equation when we know two temperatures and pressures, and the *graphical* form for three or more.

The intercept of a Clapeyron graph is not useful; its value may best be thought of as the pressure exerted by water boiling at infinite temperature. This alternative of the Clausius–Clapeyron equation is sometimes referred to as the *linear* (or *graphical*) form.

Worked Example 5.3   The Clausius–Clapeyron equation need not apply merely to boiling (liquid–gas) equilibria, it also describes sublimation equilibria (gas–solid).

Consider the following thermodynamic data, which concern the sublimation of iodine:

$T_{(sublimation)}/K$	270	280	290	300	310	320	330	340
$p_{(I_2)}/Pa$	50	133	334	787	1755	3722	7542	14 659

> We obtain the value of ΔH as 'gradient $\times -1 \times R$'.

Figure 5.13 shows a plot of ln $p_{(I_2)}$ (as 'y') against $1/T_{(sublimation)}$ (as 'x'). The enthalpy $\Delta H^{\ominus}_{(sublimation)}$ is obtained via the gradient of the graph 62 kJ mol^{-1} (note the positive sign).
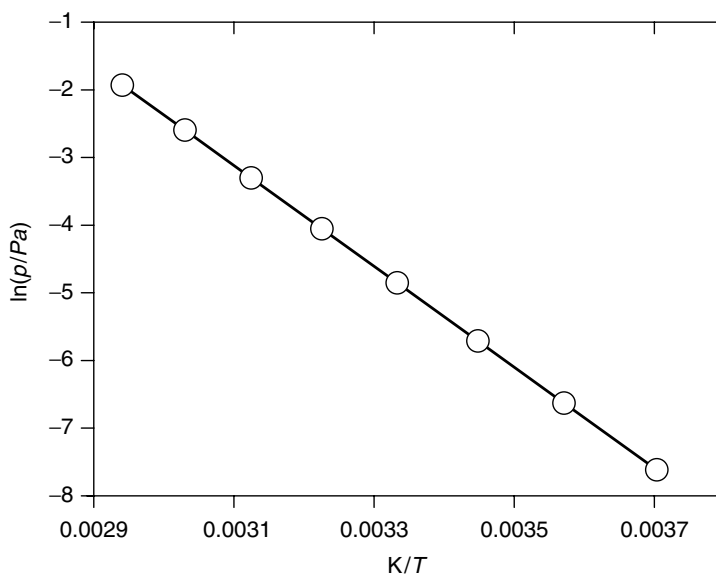

Figure 5.13   The linear form of the Clausius–Clapeyron equation: a graph of ln p (as 'y') against $1/T$ (as 'x') should be linear with a slope of $-\Delta H^{\ominus}_{(vap)} \div R$

Aside

Why does food cook faster at higher pressures?

The process of cooking involves a complicated series of chemical reactions, each of which proceeds with a rate constant of k. When boiling an egg, for example, the rate-limiting process is denaturation of the proteins from which albumen is made. Such denaturation has an activation energy E_a of about $40 \, \text{kJ} \, \text{mol}^{-1}$.

The rate constant of reaction varies with temperature, with k increasing as the temperature increases. k is a function of T according to the well-known Arrhenius equation:

> We consider the *Arrhenius equation* in appropriate detail in Chapter 8.

$$\ln \left(\frac{k \text{ at } T_2}{k \text{ at } T_1} \right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (5.7)$$

We saw in Worked Example 5.2 how the temperature of the boiling water increases from $100\,^\circ\text{C}$ to $147\,^\circ\text{C}$ in a pressure cooker. A simple calculation with the Arrhenius equation (Equation (5.7)) shows that the rate constant of cooking increases by a little over fourfold at the higher temperature inside a pressure cooker.

Boiling an egg takes about 4 min at $100\,^\circ\text{C}$, so boiling an egg in a pressure cooker takes about 1 min.

Justification Box 5.2

The Clapeyron equation, Equation (5.1), yields a quantitative description of a phase boundary on a phase diagram. Equation (5.1) works quite well for the liquid–solid phase boundary, but if the equilibrium is boiling or sublimation – both of which involve a gaseous phase – then the Clapeyron equation is a poor predictor.

For simplicity, we will suppose the phase change is the boiling of a liquid: liquid $\rightarrow$ gas. We must make three assumptions if we are to derive a variant that can accommodate the large changes in the volume of a gas:

Assumption 1: we assume the enthalpy of the phase change is independent of temperature and pressure. This assumption is good over limited ranges of both p and T, although note how the Kirchhoff equation (Equation (3.19)) quantifies changes in ΔH.

Assumption 2: we assume the gas is perfect, i.e. it obeys the *ideal-gas* equation, Equation (1.13), so

$$pV = nRT \quad \text{or} \quad pV_m = RT$$

where V_m is the molar volume of the gas.

Assumption 3: ΔV_m is the molar change in volume during the phase change. The value of $\Delta V_m = V_{m(g)} - V_{m(l)}$, where $V_{m(l)}$ is typically 20 cm^3 mol^{-1} and $V_{m(g)}$ is 22.4 dm^3 mol^{-1} (at s.t.p.), i.e. 22 400 cm^3 mol^{-1}. In response to the vast discrepancy between $V_{m(g)}$ and $V_{m(l)}$, we assume that $\Delta V_m \approx V_{m(g)}$, i.e. that $V_{m(l)}$ is negligible by comparison. This third approximation is generally good, and will only break down at very low temperatures.

First, we rewrite the Clapeyron equation in response to approximation 2:

$$\frac{dp}{dT} = \frac{\Delta H_m^{\ominus}}{T V_{m(g)}}$$

Next, since we assume the gas is ideal, we can substitute for the V_m term via the ideal-gas equation, and say $V_m = RT \div p$:

$$\frac{dp}{dT} = \frac{\Delta H_m^{\ominus}}{T} \times \frac{p}{RT}$$

Next, we multiply together the two T terms, rearrange and separate the variables, to give:

$$\frac{1}{p} dp = \frac{\Delta H_m^{\ominus}}{R} \times \frac{1}{T^2} dT$$

> We place the '$\Delta H_m^{\ominus} \div R$' term outside the right-hand integral because its value is constant.

Integrating with the limits p_2 at T_2 and p_1 at T_1 gives

$$\int_{p_1}^{p_2} \frac{1}{p} dp = \frac{\Delta H_m^{\ominus}}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

Subsequent integration yields

$$[\ln p]_{p_1}^{p_2} = -\frac{\Delta H_m^{\ominus}}{R} \times \left[\frac{1}{T}\right]_{T_1}^{T_2}$$

Next, we insert limits:

$$\ln p_2 - \ln p_1 = -\frac{\Delta H_m^{\ominus}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

And, finally, we group together the two logarithmic terms to yield the *Clausius−Clapeyron* equation:

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H^{\ominus}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$