

## Extension 10: Temperature, Kinetic Molecular Theory and Supercritical Fluids

In this extension, we start by distinguishing between heat and temperature. We re-examine the definition of temperature and introduce the Boltzmann expression which allows us to calculate the relative population of two molecular energy levels in a sample containing a large number of molecules. We move on by examining three more advanced topics. First, a more detailed examination of one aspect of the kinetic molecular theory for gases. Second, heat capacity. Thirdly, - and following on from the work on phase diagrams in the book - we explain what is meant by a supercritical fluid.

### 1. Energy and Temperature

Energy is a surprisingly difficult idea to define. Fortunately, we are more concerned with what energy 'does'. Energy has two important properties. First, **transferring energy allows us to do the activity called 'work'**. This might be by transferring energy from a fire to water to produce steam that drives a piston, or by transferring the energy of sunlight to produce electricity in a solar cell.

Second, **energy is conserved**. This means that whatever happens to energy, whatever it is converted to, the sum of the new energies always adds up to the amount of energy we started with. If we transfer  $y$  joules of energy into a dynamo to make electricity, then the sum of the energy lost as friction (heat) and electricity produced adds up to  $y$  joules. This is, of course, an alternative statement of the Law of Conservation of Energy, also known as the First Law of Thermodynamics.

At constant pressure, the energy of a material is called its enthalpy,  $H$ . The energy contained in 1 kg of iron at its melting point is double the energy contained in 0.5 kg of iron at its melting point. Quantities - like energy - which depend on the amount of substance are called *intensive* quantities. On the other hand, temperature is an *extensive* quantity: its value does not depend upon the amount of mass present. The temperature of iron at its melting point ( $1535^{\circ}\text{C}$ ) is the same whether we have 0.5, 1 or 100 kg of iron. An analogy, called 'the nail and the bath', helps to distinguish between temperature and energy. A red hot nail has a much higher temperature than a bath of lukewarm water, but the bath - because of its much greater mass - contains more thermal energy (commonly termed heat).

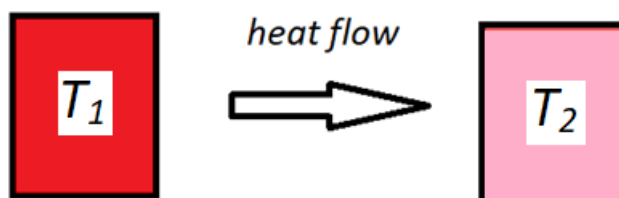
Table 1 gives several definitions of temperature. Although it might not seem obvious, they are all equivalent.

**Table 1** Definitions of temperature

1	The hotness or coldness of a body
2	The condition that determines the direction of heat flow
3	A measure of the average kinetic energy of molecules in a body
4	For a given molecular system, temperature is a quantity that controls the population of the available energy levels

Definition 1 is the one that we meet first in school. A hot object is hot to the touch and we might use a thermometer to measure the temperature of an object. The scale used on the thermometer is a matter of convenience and we will use either the Celsius scale (in degrees  $^{\circ}\text{C}$ ) or the absolute temperature scale, in kelvin (K).

Definition 2 relates to the direction of flow of heat energy. If two pieces of metal are at the same temperature, no heat energy will travel between them. Even the slightest difference in temperature will initiate the flow of heat energy and such a flow will continue until the two pieces of metal are at the same temperature. The amount of heat energy that flows depends on both the masses of the metals and upon the temperature difference between the two pieces of metal, but under no circumstances will heat energy travel spontaneously (that is, without assistance) from a cold object to a hot object. Historically, the idea that heat always flows from hot to cold has occupied a central position in scientific thought and we will return to this in Extension 16.



**Fig. 10.1** For centuries, scientists have been fascinated by the universal observation that heat flows spontaneously from a hot to a cold body, never from a cold body to a hot body. Here,  $T_1 > T_2$ .

Definition 3 relates temperature to the average kinetic energy of particles. As explained in Unit 10 of the book, the particles of a lump of matter move faster at higher temperature because they have more kinetic energy.

## 2. The Boltzmann distribution equation for the population of energy levels

Definition 4 requires explanation. Think of a container of hydrogen gas molecules. Imagine that the container is heated by a Bunsen flame. Energy is transferred to the container from the flame. There are two consequences of this heat transfer. First, both the temperature and pressure of the gas inside the container increases. Second, more hydrogen molecules occupy higher energy levels and the average kinetic energy of the gas molecules increases.

Let the number of molecules in energy level  $E_2$  and  $E_1$  be  $N_2$  and  $N_1$  respectively.  $E_2$  is greater than  $E_1$ . The **Boltzmann distribution equation**<sup>1</sup> connects the relative number of molecules at these energies (i.e. the ratio  $N_2/N_1$ ) with the temperature,  $T$  (in K), of the collection (the 'system') of molecules and the energy difference  $E_2 - E_1$ :

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/RT} \quad \dots(1)$$

Where  $R$  is the universal gas constant ( $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The units of  $E$  are  $\text{J mol}^{-1}$ . Note that the absolute values of  $E_2$  and  $E_1$  are unimportant: it is the difference  $E_2 - E_1$  that influences  $N_2/N_1$ .

<sup>1</sup> Another equation due to Boltzmann, referred to as *the Boltzmann Equation*, is discussed in Extension 16. In using equation (1) we are ignoring the fact that there might be several molecular states of the same energy. This is called degeneracy and it is discussed further in more advanced textbooks.

## EXAMPLE 1

Suppose that two energy levels are separated by  $10 \text{ kJ mol}^{-1} = 10000 \text{ J mol}^{-1}$ . Then,  $E_2 - E_1 = 10000 \text{ J mol}^{-1}$ . At 308 K, the relative population of the molecules in energy level  $E_2$  and  $E_1$  is:

$$\frac{N_2}{N_1} = e^{-(10000)/(8.3145 \times 308)} = 0.020$$

For example, suppose there are 50 molecules in energy level 1, then there will only be one molecule in energy level 2. (Check this out yourself.  $1/50 = 0.02$ ). See Fig 10.1. The relative percentage of molecules in energy level 2 compared to energy 1 is therefore:

$$\frac{0.020 \times 100}{1} = 2.0 \%$$

If we increase the temperature of the gas molecules to 1750 K, then

$$\frac{N_2}{N_1} = e^{-(10000)/(8.3145 \times 1750)} = 0.50$$

For example, if there are 34 molecules in energy level 1, there are 17 in energy level 2 (see Fig. 10.2). (Check this.  $17/34 = 0.5$ ).

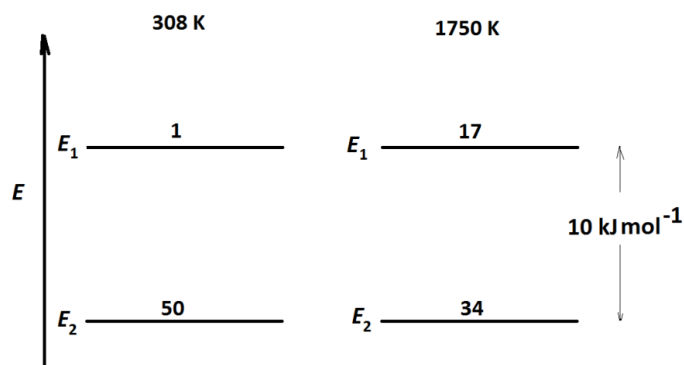
This calculation confirms that at higher temperatures, more of the higher energy levels are populated. The nature of the 'e to the power of.....' in the Boltzmann distribution equation, equation (1), means that  $\frac{N_2}{N_1}$  increases very rapidly with temperature. This is sometimes described by stating that the ratio  $N_2/N_1$  is 'very sensitive' to temperature. In our example, the temperature has increased by the ratio  $(1750/308) = 5.7$ , yet the value of  $N_2/N_1$  has increased by  $(0.5/0.02) = 25$ .

Look at the RHS of the Boltzmann distribution equation:

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/RT}$$

$E_2$  and  $E_1$  are two of the many molecular energies allowed by nature. Such energies are fixed for that molecule. Therefore, for a particular molecule, it is the temperature  $T$  that controls the distribution (or spread) of molecules in the different energy levels. This justifies the 4<sup>th</sup> definition of temperature given in table 1:

**For a given molecular system, temperature is a quantity that controls the population of the available energy levels**



**Fig. 10.2** Numbers of molecules in the higher and lower energy levels in a collection of 51 molecules and calculated using the Boltzmann equation for the case where  $E_2 - E_1 = 10 \text{ kJ mol}^{-1}$ .

The Boltzmann expression applies when the collection of molecules is at thermal equilibrium i.e. it is at a constant temperature. If, for example, the container of hydrogen is dropped into an ice bath, the molecules would exchange energy by collisions and only when the system has reached the new (lower) temperature can we equation (1) in calculations.

In the calculations above,  $\Delta E = E_1 - E_2 = 10 \text{ kJ mol}^{-1}$ . This is the typical difference between the first two vibrational energy levels in a diatomic molecule. Since  $N_2/N_1 = 0.02$ , most diatomic molecules will sit in their lowest vibrational energy levels at room temperature. The difference between the lowest electronic energy levels (energy due to the position of electrons in bonding orbitals) in diatomic molecules is typically  $200 \text{ kJ mol}^{-1}$ . Applying the Boltzmann equation at room temperature, say  $300 \text{ K}$ , we see that:

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/RT} = e^{-(200000)/(8.3145 \times 300)} = 1.5 \times 10^{-35}$$

This demonstrates that the population of the second energy is negligibly small. Even if there were one mol of molecules ( $6.022 \times 10^{23}$  molecules), it is statistically very unlikely that there would even one molecule in the second energy level. Increasing the energy gap between the energy levels has a dramatic effect in reducing the population of the higher energy level.

Why does nature follow the Boltzmann distribution of energies? It turns out for large numbers of molecules<sup>2</sup>, the Boltzmann distribution is simply a reflection of the most statistically probable distribution for that energy gap (i.e.  $E_2-E_1$ ) at that temperature. One distribution is so probable that at that temperature it is the only distribution that is ever observed<sup>3</sup>. This was proved mathematically by the famous theoretician Ludwig Boltzmann, who was born in Vienna, Austria, in 1844. Boltzmann is also remembered through the universal constant known as the Boltzmann constant,  $k$ . The Boltzmann constant and the universal gas constant ( $R$ ) are simply related:

$$k = \frac{R}{N_A}$$

Since  $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $N_A$  (Avogadro's Number) =  $6.022 \times 10^{23} \text{ mol}^{-1}$ :

<sup>2</sup> We nearly always operate with extremely large numbers of molecules. Since one mol of gas contains  $6 \times 10^{23}$  molecules, even a tiny sample of gas contains trillions of molecules.

<sup>3</sup> See Extension 16, s7, where energy distributions in large collections of molecules is discussed in greater detail.

$$k = \frac{8.3145}{6.022 \times 10^{23}} = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

It may help to think of  $R$  as the Boltzmann constant per mol of particles.

### 3. The Kinetic Molecular Theory of Gases

In Unit 10 we introduced the ideal gas equation:

$$PV = nRT \quad \dots(2)$$

where  $n$  is the number of moles of gas in the container of volume  $V$  at temperature  $T$ . Rearranging for the pressure,  $P$ , of the gas:

$$P = \frac{nRT}{V}$$

we see that the gas pressure increases as the number of mols of gas (which is proportional to the number of molecules of gas) increases.

The ideal gas equation is verified by experiment and it allows us to successfully calculate one of the parameters in its equation provide we know the others. To use it (for example, to calculate the pressure of a sample of gas from  $V$ ,  $T$  and  $n$ ) requires no theoretical model: 'the equation works' and provided that gas pressure is not too high or temperature too low its predictions are verified by experiment. **We can apply the ideal gas equation without drawing upon any unpinning theoretical model for gases.** Nevertheless, there is a remarkable feature of this equation: the pressure of a sample of gas is independent of the *type* of gas. The equation works whether the gas consists of hydrogen, benzene vapour, neon or water vapour. This is rather curious: surely a heavier molecule would thump into the container wall with greater force and cause a higher pressure?

The answer to this puzzle comes from the kinetic molecular theory. The assumptions in this theory are:

1. Gases consist of molecules in chaotic and random motion.
2. The molecules do not attract or repel each other.
3. That collisions between any two molecules does not result in an overall loss of energy (i.e. a change in temperature) of the gas sample.
4. The volume of the gas molecules is small compared to the volume of the container

Armed with these assumptions, mathematical analysis of the pressure caused by the impact of gas particles (molecules) on the surface of a container shows that at a particular temperature,  $T$ , the pressure of the gas,  $P$ , is related to:

- the number of mols of gas ( $n$ )
- the container volume  $V$
- the molar mass  $M$  of the gas
- and to  $v$ , the mean speed of the molecules<sup>4</sup>.

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<sup>4</sup> More precisely,  $c$  is a kind of average speed known as the root mean square speed of the molecules but we needn't be distracted by that here.

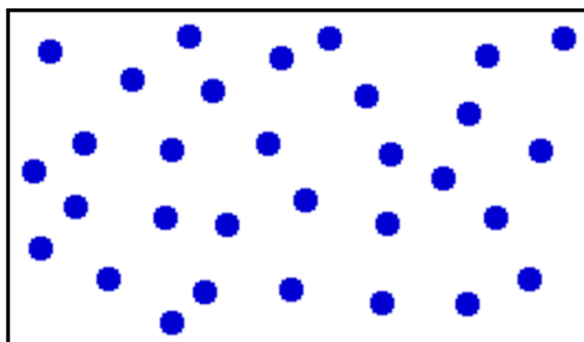
The exact relationship between these quantities is found to be:

$$P = \frac{1}{3} \frac{nMv^2}{V} \quad (3)$$

We will not derive this but the important point to note is that this equation is the result of a theoretical consideration of the way that molecules behave in a gas. **It is not an equation derived from experiment.**

Equation (3) provides a theoretical prediction that gas pressure:

- increases with the molar mass of the gas,  $M$ . Provided that nothing else changes,  $P$  doubles as  $M$  doubles.
- is inversely proportional to container volume,  $V$ . This is another statement of Boyle's Law.



**Fig. 10.3** In the mathematical analysis of the kinetic molecular theory, it is assumed that gases consist of tiny molecules travelling randomly through space. It is assumed that the molecules do not significantly attract each other.

Suppose that we have two containers of different gases at the same pressure  $P$ , for example, oxygen and nitrogen. Both containers have equal volume and contain the same number of mols of gas,  $n$ . The pressure of gas in each container,  $P_1$  and  $P_2$ , is calculated using the mathematical model of gas behaviour, equation (3):

$$P_1 = \frac{1}{3} \frac{nM_1v_1^2}{V} \quad \text{and} \quad P_2 = \frac{1}{3} \frac{nM_2v_2^2}{V}$$

Where  $M_1$  and  $M_2$  are the molar masses of the two gases and  $v_1$  and  $v_2$  are the mean speeds of the molecules of the two gases. Since we have specified that the gases are at the same pressure we can write:

$$P_1 = P_2$$

or

$$\frac{1}{3} \frac{nM_1v_1^2}{V} = \frac{1}{3} \frac{nM_2v_2^2}{V}$$

Cancelling like terms gives:

$$M_1v_1^2 = M_2v_2^2 \quad (4)$$

Equation (4) explains the observation that the pressure of a gas calculated using the ideal gas equation is independent of the mass of the molar mass of gas. Since the molecules are of different

molar mass, the right and left hand sides of equation (4) can only be equal if  $v_1$  and  $v_2$  are different. If  $M_2 > M_1$ , then for a particular pressure,  $P$ ,  $v_2$  must be less than  $v_1$  so that smaller molecules must travel faster than big molecules. In other words, the mean molecular speed of a gas consisting of a heavier molecule (higher mass) is adjusted perfectly so that the values of  $v_1^2$  and  $v_2^2$  preserve the equality of equation (4). We now have a theoretical basis to explain the independence of the predictions of equation (2), the ideal gas equation, on the type of the gas molecules present.

#### 4. Molar Heat Capacity of an Ideal Monoatomic Gas

We now look at the kinetic energy (energy due to movement) of a monoatomic molecule in the gas phase. (A monoatomic molecule is one containing one atom, such as Argon, Ar). The only source of kinetic energy of a monoatomic molecule is due to the movement of molecules through space (so-called **translational energy**). The kinetic energy,  $E_K$ , of a collection of moving particles of  $n$  mols of gas molecules is calculated by the equation:

$$E_K = \frac{1}{2}nMv^2 \quad (5)$$

or

$$2E_K = nMv^2 \quad (6)$$

where  $M$  is the molar mass of the gas and  $v$  is mean speed of the molecules. Equation (5) is simply an adaption of the familiar equation for the kinetic energy (KE) of a particle from basic physics:

$$KE = \frac{1}{2}mv^2$$

to allow for the fact that we wish to work with the amount of substance in mols rather than in number of molecules.

Rearranging equation (3) gives:

$$PV = \frac{nMv^2}{3}$$

We now combine this theoretical equation with the experimental ideal gas equation:

$$PV = nRT$$

so that

$$\frac{nMv^2}{3} = nRT$$

If we substitute  $2E_K$  for  $nMv^2$ :

$$\frac{2E_K}{3} = nRT$$

Rearrangement gives:

$$E_K = \frac{3}{2}nRT \quad (7)$$



This equation confirms our previous statement (see Table 1) that the average molecular energy of a monoatomic ideal gas increases with temperature. If we double  $T$ , then  $E_K$  doubles.

Think of 1 mol of gas at 298 K. Its kinetic energy is easily calculated using equation (7):

$$E_K = (3/2) \times 8.3145 \times 298 = 3716.5 \text{ J or } 3.7165 \text{ kJ mol}^{-1}.$$

If the gas temperature is raised to 299 K, its kinetic energy is greater:

$$E_K = (3/2) \times 8.3145 \times 299 = 3729.1 \text{ J}$$

The amount of energy needed to raise the temperature of 1 mol of gas from 298 K to 299 K is therefore:

$$3729.1 - 3716.5 = 12.6 \text{ J.}$$

The amount of energy needed to raise the temperature of 1 mol of a substance by 1 degree °C (or K) is called its **molar heat capacity**. The units of heat capacity are  $\text{J K}^{-1} \text{ mol}^{-1}$ . For gases, we need to specify that the heat is added at constant volume i.e. that the gas is not allowed to expand during the absorption of heat: the molar heat capacity is then described as 'heat capacity at constant volume' and is symbolized  $C_v$ :

$$C_v \text{ of an ideal monoatomic gas} = 12.6 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Heat capacity may be likened to sponges absorbing water. Think of two sponges made of different materials. Droplets of water are added to both sponges. The one sponge is very absorbent and the water enters its structure so that no water appears at its surface. The other is not. Now think of two substances and replace the added water with heat and the appearance of surface water with the temperature of the substance. The higher the molar heat capacity of a substance, the higher is its ability to absorb ('use up') heat energy inside its structure and so minimise an increase in its own temperature.

Here are some experimentally determined  $C_v$  values ( $\text{J K}^{-1} \text{ mol}^{-1}$ ) for the noble gases:

Helium	12.5
Neon	12.5
Argon	12.5

The values are very close to that predicted for an ideal gas:  $12.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . The agreement between the value of  $C_v$  predicted by the kinetic molecular theory and that observed experimentally is excellent. Despite the fact that the assumptions of the kinetic molecular theory are unrealistic (we know, for example, that molecules have volume), the model successfully predicts the molar heat capacities of gases whose molecules consist of only one atom.

With molecules containing two or more atoms (such as  $\text{H}_2$  and  $\text{H}_2\text{O}$ ) agreement between the predicted and experimental values is poor. This is because equation (7) applies only to monoatomic gases where the only kinetic energy of a molecule is due to its movement through space (translational energy). For molecules with more than one atom, there are other contributions to the kinetic energy of the molecule. Molecules can rotate and vibrate and these motions also store kinetic energy.



It is important not to get 'too bogged down' by the above equations. Introducing them has a simple purpose and this glimpse of the mathematics of an ideal gas serves to illustrate how experimental observations - i.e. the ideal gas law - may be rationalized using a theoretical model. Here, the theoretical model reproduces the predicted mathematical behaviour of the variables ( $P$ ,  $V$ ,  $n$ ,  $T$ ) in the ideal gas equation. But the theoretical model also explains why (for example), the ideal gas equation works independently of the type of gas and it also allows us to predict why the heat capacity of monoatomic gases is about  $12.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . Similar mathematical models mimic the behaviour of other 'systems' in chemistry, and they allow the calculation of reaction rates, equilibrium constants and bond energies from first principles.

## 5. Supercritical Fluids

In unit 10 we defined critical pressure and critical temperature. Although we might think that a gas could always be liquefied – whatever its temperature – if enough pressure is applied, experiments show that for each gas **there is a critical temperature above which liquefaction is impossible** – even at the highest available pressures. The pressure required to liquefy a gas at its **critical temperature** is called its **critical pressure**.

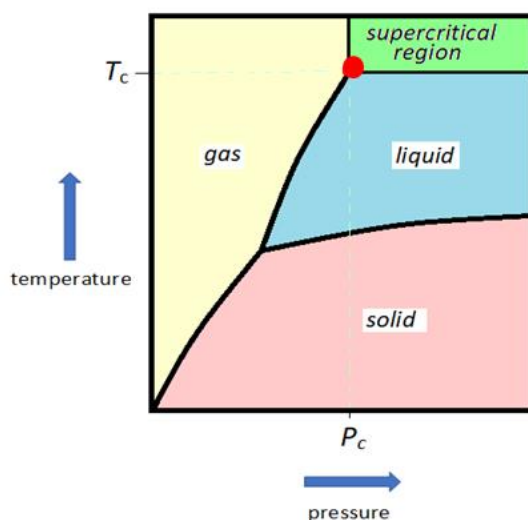
For example, the critical temperature of carbon dioxide is  $31^\circ\text{C}$  (304 K). Above this temperature, even a pressure of 100,000 atm would not produce liquid  $\text{CO}_2$ . At  $31^\circ\text{C}$ , a pressure of 74 atm is required to produce liquid  $\text{CO}_2$ . Therefore, for  $\text{CO}_2$ :

- Critical temperature ( $T_c$ ) is 304 K: this is the highest temperature at which liquid  $\text{CO}_2$  can exist.
- Critical pressure ( $P_c$ ) is 74 atm: this is the pressure needed to liquefy  $\text{CO}_2$  at its critical temperature of 304 K

In Unit 10 we introduced the generalized phase diagram for the solid, liquid and gaseous phases of a pure solid, such as water or carbon dioxide. Fig. 10.4 shows the diagram again but with the pressure and temperature extended to higher values. At temperature/pressure coordinates within the yellow zone, the most stable phase of  $\text{CO}_2$  is gas; within the blue region it is  $\text{CO}_2$  liquid that is the most stable; in the pink region it is solid  $\text{CO}_2$  that is the most stable.

Fig. 10.4 also shows the critical pressure and temperature of the substance under study. The co-ordinate point  $T_c$ ,  $P_c$  is called the **critical point** of the substance.

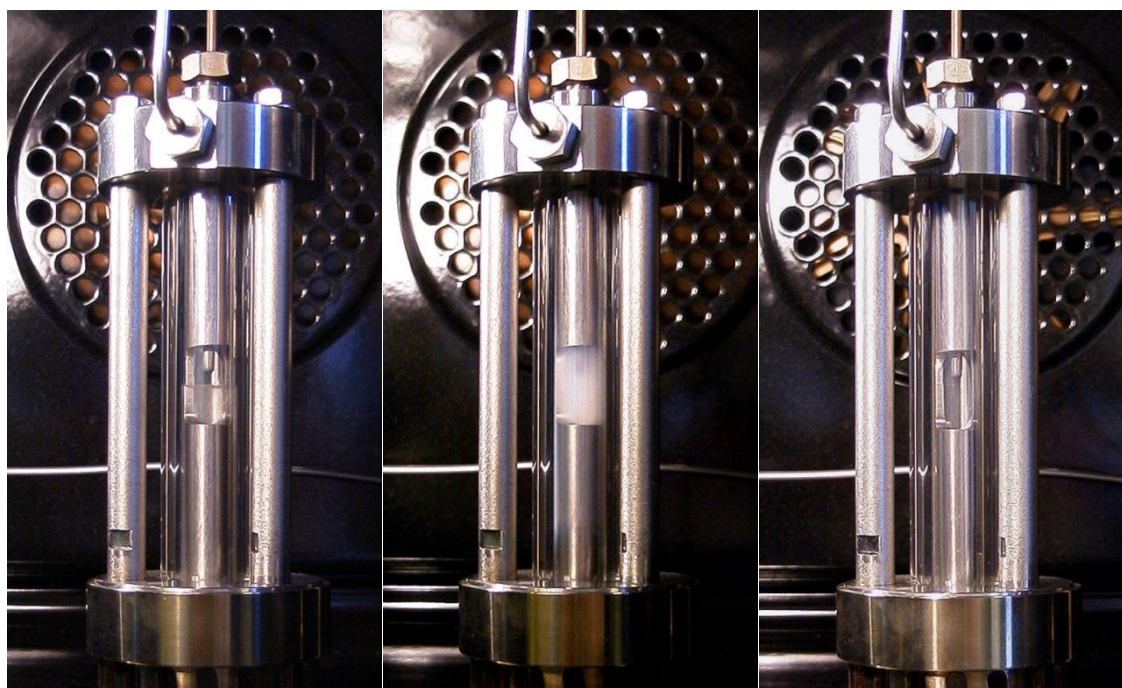
At temperatures above the critical temperature and above the critical pressure (a region of pressures and temperatures shown in Fig. 10.4 as a green box) the substance is said to be a **supercritical fluid**: here, the word 'super' means 'above' i.e. the supercritical fluid only exists above its critical pressure and critical temperature.



**Fig. 10.4** Generalised phase diagram showing the supercritical region. The red dot ● is the critical point.  $T_c$  and  $P_c$  are the critical temperature and critical pressure respectively.

Ethane,  $C_2H_6$ , is a colourless gas at room temperature and pressure. Fig. 10.5 shows some remarkable photographs of ethane (taken by Dr. Sven Horstmann, Laboratory for Thermophysical Properties, Germany). At or close to the critical point, fluids become opaque and white (a phenomena given the grand name 'critical opalescence') and this is seen in Fig. 10.5(b).

Substances in the supercritical region are neither gases or liquids and their density is intermediate between that of the liquid and gas states. They therefore spread out (diffuse) in a similar way to (but less effectively than) a gas and they act as solvents in a similar way to (but less effectively than) a liquid. High diffusion rates and solvation (dissolving) power are both highly desirable in solvent extraction and so the use of supercritical fluids in solvent extraction effectively incorporates both these properties in the solvent. Increasing the pressure of the supercritical fluid increases its solvating power but reduces its rate of effusion. The use of supercritical fluids to extract solutes from organic material is called **supercritical fluid extraction** (SFE). This subject was introduced in the book on page 381 where the decaffeination of coffee was also discussed. Special equipment is needed to maintain the solvent in a supercritical state. Since SFE requires that the solvent is above its critical temperature some heating is often required (although in the case of  $CO_2$  this is minimal since its critical temperature is only  $31^\circ C$ ). The requirement that the solvent be above its critical pressure is usually more demanding as pressure-resistant vessels are required (for  $CO_2$   $P_c = 74$  atm). We do not usually require an exact temperature or pressure to be maintained, provided that both  $P_c$  and  $T_c$  are exceeded during the extraction.



(a)

(b)

(c)

**Fig. 10.5** Ethane in a pressure container. In (a), the ethane gas is pressurised below its critical temperature and both (clear) liquid and gas co-exist; (b) is the same ethane sample but exactly at its critical temperature of  $32.17\text{ }^{\circ}\text{C}$  and at its critical pressure of  $48.72\text{ bar}$ . The system is now uniformly opaque and since there is only one phase and there is no meniscus; (c) shows the sample of ethane above its critical point. The fluid is clear. The ethane is neither gas or liquid: it is said to be in the supercritical state. Photographs kindly provided by Dr. Sven Horstmann.

## 6. The Reasons Why Carbon Dioxide is a Useful Solvent

Supercritical carbon dioxide is a particularly useful solvent because:

1. It is easily removed (leaving the extracted material behind) because it will evaporate in the open lab.
2. It is reasonably good solvent for non-polar or slightly polar solutes. This makes supercritical  $\text{CO}_2$  a good solvent for a wide range of organic compounds, including most hydrocarbons. In the case of caffeine (in coffee beans), supercritical  $\text{CO}_2$  is able to extract (i.e. dissolve) caffeine without extracting the bigger (and less soluble) molecules that give coffee (and roasted coffee) its characteristic taste.
3. Experiments show that supercritical  $\text{CO}_2$  is a good solvent even in the presence of water. This is important as water is often present in mixtures containing the solute that we wish to extract. (The temperature required to maintain a mixture of  $\text{CO}_2$  and water in its supercritical state is higher than  $31\text{ }^{\circ}\text{C}$ , but is easily achieved experimentally).
4. The low critical temperature of  $\text{CO}_2$  means that organic compounds are less likely to be decomposed.
5. Carbon dioxide is non-toxic. For example, if halogen-containing solvents were used to extract caffeine from coffee beans, there is the danger that traces of toxic solvent might be present in packaged coffee beans.