GASES

OBJECTIVES

Aims
In this chapter you will study the simple model of an ideal gas and examine some of the ways a real gas differs from an ideal gas and the consequences of these differences. You should learn to appreciate the presentation of information about the behaviour of gases on a pressure-volume diagram and how to use such a presentation to describe changes in the gas.

Minimum Learning Goals
When you have finished studying this chapter you should be able to do all of the following.

1. Explain, interpret and use the following terms
   *ideal gas, critical point, maximum inversion temperature, free expansion, throttling, gas, vapour, partial pressure, saturated vapour pressure; dew point.*

2. Recall and apply the equation of state for an ideal gas: sketch isotherms on a $PV$ graph.

3. Sketch, discuss and interpret isotherms for a real gas.

4. Use the first law and the equation of state to describe and calculate the behaviour of gases during adiabatic and isothermal changes.

5. Describe free expansion and throttling of a gas and discuss the energy changes and flows involved; describe how throttling can be used in the liquefaction of gases.

6. Describe boiling and dew formation.

PRE-LECTURE

The topics summarised below were covered in TP3 for gases, liquids and solids. Here they are restricted to gases.

7.1 INTERNAL ENERGY OF A GAS

The internal energy, $U$, of a gas consists of kinetic energy ($U_{\text{KIN}}$) and potential energy ($U_{\text{POT}}$).

Internal kinetic energy ($U_{\text{KIN}}$) is associated with the translational, rotational and vibrational motions of molecules. Changes in $U_{\text{KIN}}$ mean changes in temperature.

Internal potential energy ($U_{\text{POT}}$) is associated with the weak attractive forces between molecules and with the vibrations of the molecules. Changes in $U_{\text{POT}}$ are not associated with changes in temperature.

There is also potential energy associated with the strong chemical binding forces within molecules: $U_{\text{chem}}$. Since in our study no chemical changes will be involved, we do not need to take it into account here.

An ideal gas is made up of atoms with no attractive force between them (except when they collide). $U_{\text{KIN}}$ connected with translational motion is the only form of internal energy for an ideal gas.

We can write

$$U = U_{\text{KIN}} + U_{\text{POT}} \quad \text{(Real gas)} = U_{\text{KIN}} \quad \text{(Ideal gas)}$$

7.2 THE FIRST LAW OF THERMODYNAMICS

$$\Delta U = Q + W,$$

where $Q$, the heat flow to or from the system, is positive when heat flows into the system and $W$, the work done on or by the system, is positive when work is done on the system.
Work done on a gas

The work done on a gas as it changes volume from \( V_1 \) to \( V_2 \) is

\[
W = - \int_{V_1}^{V_2} P \, dV,
\]

and, if the pressure is constant during the change,

\[
= -P \, (V_2 - V_1).
\]

If the volume increases, that is \( P \, (V_2 - V_1) > 0 \), then \( W < 0 \) and work is done by the gas;

if the volume decreases, that is \( P \, (V_2 - V_1) < 0 \), then \( W > 0 \) and work is done on the gas.

Units

The unit of pressure is the pascal, abbreviation Pa.

\[
1 \text{ Pa} = 1 \text{ N.m}^{-2}
\]

The kilopascal, kPa, is a commonly used multiple of the pascal.

Atmospheric pressure \( = 101 \text{ kPa} = 1.01 \times 10^5 \text{ N.m}^{-2} \).

7.3 IDEAL GAS

If the density of a gas is low enough it obeys simple laws which were first discovered experimentally in the 17th. and 18th centuries.

1. Boyle's Law: For a constant amount of gas at a constant temperature \( T \), the product of pressure \( P \) and volume \( V \) is a constant:

\[
P V = \text{constant}.
\]

2. Charles' Law: For a constant amount of gas at a constant pressure, the ratio of volume to temperature is a constant:

\[
\frac{V}{T} = \text{constant}.
\]

These laws can be combined to give the ideal gas law: For a constant amount of gas

\[
\frac{PV}{T} = \text{constant}.
\]

Equation of State

For a mole of any gas \( (6.02 \times 10^{23} \text{ molecules}) \) the last-mentioned constant, which is called the universal gas constant \( R \), has the value \( 8.31 \text{ J.K}^{-1}.\text{mol}^{-1} \).

Consequently if the amount of gas is \( n \),

then \( PV = nRT \).

This is called an equation of state as it gives a relationship among the properties \( P, V, T \) and \( n \) for any equilibrium state of a gas.

A hypothetical gas which would obey this equation under all circumstances is called an ideal gas. Real gases obey this equation well only if their density is low enough. However the ideal gas equation of state is often used as an approximation to real gas behaviour.

The relation among \( P, V, T \) for an ideal gas depends only upon the number of molecules: the details of the structure of the molecules are irrelevant. Thus we would expect a gas consisting of a large number of minute solid balls to also obey the ideal gas equation of state. The proof of this expectation is one of the basic calculations of the subject of kinetic theory, which attempts to understand the properties of matter starting with the assumption that it consists of large numbers of particles and with a knowledge of the way these particles interact with each other.

Demonstration of an ideal-gas model

The motion of steel ball bearings in a vibrating dish is shown on the videotape as a representation of the motion of molecules in an ideal gas.
7.4 ISOTHERMS

Ideal gas

For a given mass of ideal gas, provided \( T \) is constant, the product \( PV \) is constant. Therefore when pressure is plotted as a function of volume (with temperature constant) an hyperbola is obtained. Each point on the curve represents a state of the gas at that temperature: the curve is called an isotherm. For a different value of temperature we obtain a different isotherm (hyperbola).

![Figure 7.1 PV diagram for an ideal gas](image)

Real gas

![Figure 7.2 PV diagram for a real gas (carbon dioxide)](image)

On the far right of the graph, where the volume is large and density low we expect ideal gas behaviour. If we follow the 21°C isotherm in from this region we find that the volume decreases as the pressure increases until point A is reached. Here, without any change in pressure there is a big decrease in volume as the gas condenses to the liquid phase. At point B all the gas has condensed, and from here on a large increase in pressure is required to produce even a small decrease in volume. As the temperature is increased the volume change on condensation decreases until for a temperature of 30.9°C there is no change in volume on condensation. This temperature is called the critical temperature and point C the critical point. At temperatures lower than the critical temperature an increase in pressure will eventually cause a gas to condense to the liquid phase; at higher temperatures, no amount of compression will produce condensation. A gas at a temperature less than its critical temperature is usually called a vapour.

<table>
<thead>
<tr>
<th>Critical Temperatures</th>
<th>At Room Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>helium</td>
<td>5.3 K</td>
</tr>
<tr>
<td>hydrogen</td>
<td>33.2 K</td>
</tr>
<tr>
<td>oxygen</td>
<td>154 K</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>304 K</td>
</tr>
<tr>
<td>water</td>
<td>647 K</td>
</tr>
<tr>
<td>mercury</td>
<td>1900 K</td>
</tr>
</tbody>
</table>
7.5 IDEAL GAS MODEL - WHAT IS MISSING?
In the ideal gas model, molecules interact only when they collide with each other; at other times, each molecule moves uninfluenced by the presence of the other molecules. For real gases however, there are weak attractive forces called Van der Waals forces between the molecules. From the graph below of the force between two molecules as a function of separation (see also FE2), we see that for small separations there is strong repulsion; as the separation increases the force becomes attractive and its magnitude decreases as the inverse of the seventh power of the separation.

![Figure 7.3 Graph of intermolecular force](image)

As the pressure of a mass of gas is increased, the average distance between molecules decreases, hence the attractive force increases and may eventually curtail the translational motion of the molecules: the gas then condenses to a liquid.

7.6 FREE EXPANSION
In a free expansion, a gas is allowed to expand into an evacuated vessel.

![Figure 7.4 Free expansion](image)

No external work is done in a free expansion \([W = 0]\). In addition, if the free expansion occurs under adiabatic conditions there is no heat flow \([Q = 0]\). The first law of thermodynamics then tells us that under these constraints \(\Delta U = 0\).

When an ideal gas undergoes a free expansion, since \(\Delta U = 0\), there is no change in \(U_{\text{KIN}}\) and there is thus no change in temperature.

When a real gas undergoes a free expansion the average separation of the molecules is increased and, since there is an attractive force between these molecules, \(U_{\text{POT}}\) is increased. Since \(\Delta U = 0\), \(U_{\text{KIN}} + U_{\text{POT}}\) remains unchanged during a free expansion (see pre-lecture material). Thus, after the free expansion of a real gas, \(U_{\text{KIN}}\) and the temperature must decrease. There is a decrease in temperature as a result of a free expansion of a real gas.
7.7 THROTTLING

Throttling occurs when a gas flows, under adiabatic conditions, from one region at a constant pressure to another region at a lower constant pressure (the flow could be through a porous wall, as below, or through a valve).

\[
\text{Throttling } (P_1 > P_2)
\]

Net work done on gas = \( P_1 \frac{V_1}{P_2 V_2} \)

**Figure 7.5 Throttling process**

The energy interchanges in the throttling process occur as follows.

Initially all the gas is on the high pressure side with pressure \( P_1 \) and volume \( V_1 \). As the gas diffuses through the porous wall, the piston moves in such a way as to keep the pressure on that side constant at \( P_1 \). The work done on the gas by the force exerted on this piston will be given by the product of the constant pressure \( P_1 \) and the change in volume; when all the gas has been transferred this product is \( P_1 V_1 \).

The piston on the other side moves outwards to keep the pressure there constant at \( P_2 \). Finally all the gas is on the low pressure side and occupies a volume \( V_2 \). The work done by the expanding gas on this side on its surroundings will be given by the product of the constant pressure \( P_2 \) and the change in volume; when all the gas has been transferred this product is \( P_2 V_2 \).

Hence the net work done on the gas during this throttling is \( P_1 V_1 - P_2 V_2 \). Because of the adiabatic boundaries, there is no heat flow and so the first law gives:

\[
\Delta U = U_2 - U_1,
\]

\[
= P_1 V_1 - P_2 V_2.
\]

As

\[
U = U_{\text{KIN}} + U_{\text{POT}},
\]

we can write, with some rearrangement,

\[
U_{2\text{KIN}} - U_{1\text{KIN}} = (U_{1\text{POT}} - U_{2\text{POT}}) + (P_1 V_1 - P_2 V_2).
\]

Because the average distance between molecules is greater on the low pressure side, than on the high pressure side, \((U_{1\text{POT}} - U_{2\text{POT}})\) is always negative. However, since we do not know the value of \( (P_1 V_1 - P_2 V_2) \), we can make no general conclusion about the sign of \( (U_{2\text{KIN}} - U_{1\text{KIN}}) \) and therefore about the temperature increases or decreases.

It is found experimentally that temperature changes on throttling follow these two generalizations.

(a) If the initial temperature is high enough, throttling always leads to an increase in temperature.

(b) If the initial temperature is below a certain value, called the maximum inversion temperature, throttling may lead to cooling provided the pressure difference is large enough.
The following table lists the maximum inversion temperature for several gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Maximum Inversion Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>helium</td>
<td>51 K</td>
</tr>
<tr>
<td>hydrogen</td>
<td>204 K</td>
</tr>
<tr>
<td>nitrogen</td>
<td>621 K</td>
</tr>
<tr>
<td>oxygen</td>
<td>893 K</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>1 500 K</td>
</tr>
</tbody>
</table>

**Demonstration**

The videotape shows carbon dioxide being throttled using a CO₂ fire extinguisher. At room temperature carbon dioxide is below its maximum inversion temperature and so we expect cooling to occur. A damp cloth placed on the extinguisher nozzle freezes, indicating this anticipated reduction in temperature.

### 7.8 LIQUEFACTION

As a result of their much smaller volume, liquids are easier to transport and to store than are gases. Hence liquefaction of gases is an important component of the chemical industry. The simplest way to liquefy a gas is to increase the pressure on it. However we have seen that this would not be successful if the ambient temperature of the gas were above its critical temperature. Throttling may be used to lower the temperature of a gas to its critical temperature if the gas is at a temperature lower than its critical point. The gas can then be liquefied by increased pressure or by further throttling. The following process may be used to first cool and then to liquefy the gas. The procedure is described under the diagram.

![Diagram of liquefaction process](image)

**Figure 7.6 Use of throttling and counter-flow to liquefy a gas**

Gas, initially at a temperature below its maximum inversion temperature is maintained at a high pressure by a compressor. It passes through a throttling valve to a low pressure region. If initially the temperature drop is not sufficient to produce liquefaction, the gas is directed back to the compressor, on its way passing and cooling the incoming gas. This process (which is called counter-flow and is an example of positive feedback) is continued until the gas temperature is low enough for the gas to liquefy after passing through the throttling valve or for it to be liquefied by increased pressure.
7.9 COMPARISON OF THROTTLING AND FREE EXPANSION
You should be clear as to the difference between free expansion and throttling.

(i) They both involve movement of gas from one region to another.

(ii) In free expansion, the work done is zero. In throttling the work done is non-zero.

(iii) Free expansion (of a real gas) is accompanied by a decrease in temperature. In throttling the gas may cool or warm depending on the value of $U_2^{\text{kin}} - U_1^{\text{kin}}$.

7.10 QUESTIONS

Q7.1 Is there a temperature change in the free expansion of an ideal gas?

Q7.2 When discussing throttling we applied the first law of thermodynamics to a fixed mass of gas as it underwent the throttling process:

$$U_2 - U_1 = P_1 V_1 - P_2 V_2.$$  
Show that the initial and final values of the enthalpy for this mass of gas are the same.

Q7.3 A car tyre is pumped to a pressure of $1.7 \times 10^2$ kPa above atmospheric pressure ($1.0 \times 10^2$ kPa) when the air temperature is $20^\circ$C. After a considerable period of travel, the pressure of gas in the tyre was found to be $2.1 \times 10^2$ kPa above atmospheric pressure.

What is the temperature of the tyre? (Assume that there has been no appreciable change in the tyre volume and that the air behaves as an ideal gas.)

Why does the tyre become warm?

7.11 PARTIAL PRESSURE
Often we are interested in mixtures of gases (air for example) rather than pure gases. The pressure which any component of the mixture would exert, if it were the only component present, is called the partial pressure of the component. The total pressure is the sum of the partial pressures.

This follows directly from the equation of state of an ideal gas

$$P = \frac{n R T}{V}$$

$$= \frac{(n_1 + n_2 + n_3 + \ldots) R T}{V}$$

$$= \frac{n_1 R T}{V} + \frac{n_2 R T}{V} + \frac{n_3 R T}{V} + \ldots$$

$$= P_1 + P_2 + P_3 + \ldots$$

when $n_1$, $n_2$, and $n_3$ are the amounts of each of the individual ideal gases.
7.12 MORE QUESTIONS

Q 7.4 If dry air at a pressure of 100 kPa (atmospheric pressure) is 78.09% nitrogen, 20.95% oxygen, 0.93% argon and 0.03% carbon dioxide (by amount), what is the partial pressure of each component?

Note that the sum of the partial pressures is, of course, equal to the total pressure of the mixture.

Q 7.5 At sea level, atmospheric pressure is approximately 100 kPa and the temperature is about 300 K. Air is 20% oxygen by volume and behaves as an ideal gas. The volume of air inhaled in a breath is about half a litre \(\left(0.5 \times 10^{-3} \text{ m}^3\right)\).

What amount of oxygen is inhaled in that breath?

Compare this with oxygen inhaled in one breath at the top of Mt Everest (where the altitude is 9 km, the total pressure 30 kPa and the temperature 230 K). Assume that the volume of air inhaled here is the same as at sea level.

Q 7.6 Flight regulations usually require the provision of artificial oxygen supplies for operations above about 3000 m. Compare the amount of oxygen available per breath at this altitude (total pressure 70 kPa, temperature 279 K) with that available at sea level.

<<

7.13 EQUATION OF STATE FOR REAL GASES

The best known of these is the Van der Waals equation

\[
(P + \frac{a}{v^2})(v - b) = RT
\]

where \(v (=v/n)\) is the molar volume and where \(a\) and \(b\) are constants which depend upon the gas: \(a\) depends on the force between the molecules, \(b\) depends on the finite size of the molecules. >>

7.14 SATURATED VAPOUR PRESSURE

When point A (refer back to the real-gas isotherms diagram) was reached, the vapour began to condense. All the points between A and B correspond to states at 21°C for which vapour and liquid can exist together in equilibrium. Notice that all these states have the same value of pressure. Along this line the vapour is said to be saturated and the pressure along this line is called the saturated vapour pressure (s.v.p.). Whenever vapour is in equilibrium with its liquid phase the pressure of the vapour will equal the s.v.p. for the particular value of temperature pertaining. From the diagram we can see that the s.v.p. decreases as the temperature decreases.

The water vapour in the atmosphere is usually not saturated (i.e. its pressure is less than the s.v.p. for the temperature of the atmosphere).
Dew formation

![Figure 7.7 Isotherms for water: 25°C and 20°C](image)

We can see from these water vapour isotherms that the s.v.p. of water is 3.2 kPa at 25°C and drops to 2.3 kPa at 20°C. As the temperature drops at night, the s.v.p. decreases while the actual amount of water vapour and the partial pressure of that vapour stay the same; the vapour can easily become saturated. As the temperature falls lower still, water begins condensing from the air and is deposited on the ground (dew). The temperature at which water begins to condense from the air is called the **dew point**. The dew point will depend upon the air temperature and how much water vapour is present in the air. If the ground temperature falls low enough, the dew may freeze (frost).

Water boils when its vapour pressure equals the external pressure

![Figure 7.8 Isotherm for water: 100°C](image)

At the usual atmospheric pressure of 101 kPa the 100°C isotherm is appropriate. The external pressure falls with increasing altitude, so at these altitudes lower temperature isotherms describe the boiling process. For water to boil at room temperature the external pressure would have to be as low as 2 to 3 kPa.

The critical temperature of water, above which the vapour cannot be liquefied by increasing the pressure is 374°C. Its critical pressure is 22 MPa.