

# THE KINETIC THEORY

## 5.1. ASSUMPTIONS OF THE KINETIC THEORY

As early as 1738, Daniel Bernoulli (1700 – 1782) envisioned gaseous molecules in ceaseless motion striking the walls of their container and thereby exerting pressure (Whitten, et al., 2004). In 1857, Rudolph Clausius (1822 – 1888) published a theory that attempted to explain various experimental observations that had been summarized by Boyle's, Dalton's and Avogadro's laws (Whitten, et al., 2004).

The kinetic model of gases is based on three basic assumptions as indicated by Atkins & dePaula (2006), Ramsden (2000) & Whitten et al., (2004):

Gases consist of discrete (**separate**) molecules.

- The gas consists of molecules of mass,  $m$  in ceaseless random, straight-line motion with varying velocities. This continues until they collide with each other or the walls of the container. The molecules exert no forces on each other (except when they collide).
- The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions. Alternatively, the individual molecules are very small and are very far apart relative to their own sizes
- The molecules interact only through brief, infrequent, and elastic collisions. The total energy is conserved during a collision, that is, there is no net energy gain or loss.

An elastic collision is a collision in which the total translational kinetic energy of the molecules is conserved (Atkins & dePaula, 2006).

### 5.1.1. REAL GASES: DEVIATIONS FROM IDEALITY

When referring to ideal gases, the identity of a gas does not affect how it behaves, and the same equations should work equally well for all gases. Under ordinary conditions most real gases do behave ideally; their P and V are predicted by the ideal gas laws, so they do obey the postulates of the kinetic theory.

According to the kinetic model, (1) all but a negligible volume of a gas sample is empty space, and (2) the molecules of ideal gases do not attract one another because they are so far apart relative to their own sizes.

Under some conditions, however, most gases can have pressures and or volumes that are not accurately predicted by the ideal gas laws. This tells us that they are not behaving entirely as postulated by the kinetic theory.

Non ideal gas behaviour (deviation from the predictions of the ideal gas laws) is most significant at high pressures and/or low temperatures, that is, near the conditions under which the gas liquefies.

Johannes van der Waals (1837 – 1923) studied deviations of real gases from ideal behaviour. In 1867, he empirically adjusted the ideal gas equation (which took into account two complicating factors).

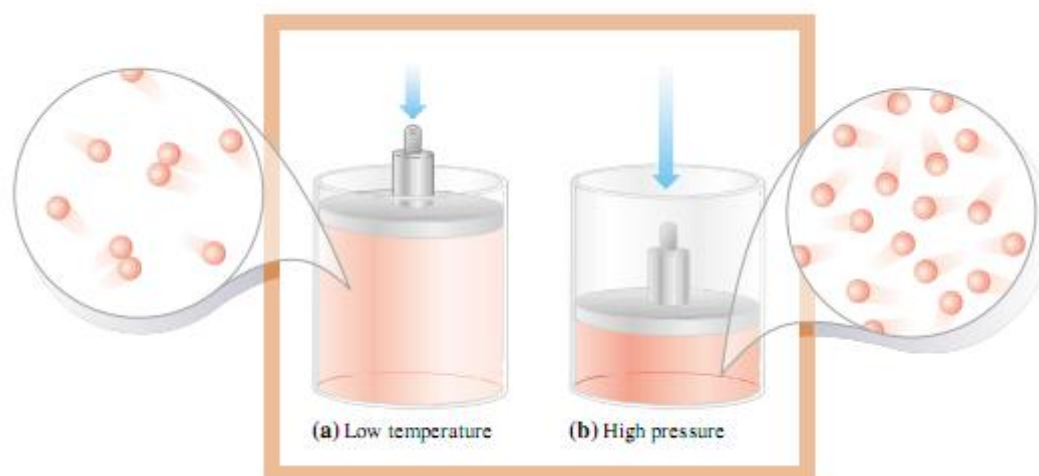
$$P_{\text{ideal}}V_{\text{ideal}} = nRT$$

### 5.1.2. A MOLECULAR INTERPRETATION OF DEVIATIONS FROM IDEAL BEHAVIOUR

Picture the following (by considering the diagram below):

(a) A sample of gas at a low temperature. Each sphere represents a molecule. Because of their low kinetic energies, attractive forces between molecules can now cause a few molecules to 'stick together'.

(b) A sample of gas under high pressure. The molecules are quite close together. The free volume is now a much smaller fraction of the total volume.



**Figure 1 –**

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#### 5.1.2.1. VOLUME

According to the kinetic theory, the molecules are so small, relative to the total volume of the gas, that each molecule can move through virtually the entire measured volume of the container,  $V_{\text{measured}}$ . But under high pressures, a gas is compressed so that the volume of the molecules themselves becomes a significant fraction of the total volume occupied by

the gas. As a result, the available volume,  $V_{\text{available}}$ , for any molecule to move in is less than the measured. To account for this we subtract a correction factor,  $nb$ .

Where:

- $n$  = number of moles
- $b$  = van der Waals coefficient

Don't worry about this coefficient; it's just a value that is specific for each gas. Therefore, if there is a decrease in the volume, we can write:

$$V_{\text{ideally available}} = V_{\text{measured}} - nb$$

The factor  $nb$  corrects for the volume occupied by the molecules themselves. **Larger molecules have greater values of  $b$ , and the greater the number of molecules in a sample (higher  $n$ ), the larger is the volume correction.** The correction term becomes negligibly small, however, when the volume is large.

### 5.1.2.2. PRESSURE

The kinetic theory describes pressure as resulting from the molecular collisions with the walls of the container. This theory assumes that attractive forces between molecules are insignificant. For any real gas, the molecules can attract one another. But at higher temperatures, the potential energy due to intermolecular attractions is negligibly small compared with the high kinetic energy due to the rapid motion of the molecules and to the great distances between them. When the temperature is quite low (low kinetic energy), the molecules move so slowly that the potential energy due to even small attractive forces does become important. This perturbation becomes even more important when the molecules are very close together (at high pressure). As a result, the molecules deviate from their straight – line paths and take a longer time to reach the walls, so fewer collisions take place in a given time interval. Furthermore for a molecule about to collide with the wall, the attraction by its neighbours causes the collision to be less energetic than it would otherwise be. As a consequence, the pressure that gas exerts,  $P_{\text{measured}}$ , is less than the pressure it would exert if attractions were truly negligible,  $P_{\text{ideally exerted}}$ . To correct for this, we subtract a correction factor,  $a(n/V)^2$ , from the ideal pressure.

$$P_{\text{measured}} = P_{\text{ideally exerted}} - a \left( \frac{n}{V_{\text{measured}}} \right)^2$$

Where:

- $n$  = number of moles
- $a$  = van der Waals coefficient
- $P$  and  $V$  are the pressure and volumes of the gas

' $a$ ' is another van der Waals coefficient that you don't really need to worry about either!

In this correction term, large values of  $a$  indicate strong attractive forces. When more molecules are present (greater  $n$ ) and when the molecules are close together (smaller  $V$  in

the denominator), the correction term becomes larger. The correction becomes negligibly small, however, when the volume is large.

When we substitute these two expressions for corrections into the ideal gas equation, we obtain the equation:

$$p = \frac{nRT}{V - nb} - a \left(\frac{n}{V}\right)^2$$

This is known as the van der Waals equation! You don't really need to remember this but it'll do you good especially in first year chemistry courses. In fact, I don't understand why CAPE doesn't teach you this, because it's just a matter of plugging in values and arriving at an answer.

Let's consider an example to illustrate the difference between the van der Waals equation and the ideal gas equation. Consider acetylene gas sample of one mole of placed in a 20.0 L container at 25 °C.

**The pressure using the Ideal Gas Law is shown to be:**

$$\begin{aligned} p &= \frac{nRT}{V} \\ &= \frac{(1 \text{ mol})(0.0821 \text{ L atm mol}^{-1}\text{K}^{-1})(298 \text{ K})}{20.0 \text{ L}} \\ &= 1.223 \text{ atm} \end{aligned}$$

**The pressure using the van der Waals equation is shown to be:**

$$\begin{aligned} p &= \frac{nRT}{V - nb} - a \left(\frac{n}{V}\right)^2 \\ &= \frac{(1 \text{ mol})(0.0821 \text{ L atm mol}^{-1}\text{K}^{-1})(298 \text{ K})}{20.0 \text{ L} - (1 \text{ mol})(0.05136 \text{ L mol}^{-1})} - (4.390 \text{ L atm mol}^{-1}) \left(\frac{1 \text{ mol}}{20.0 \text{ L}}\right)^2 \\ &= 1.215 \text{ atm} \end{aligned}$$

**Where:**

- $a = 0.05136 \text{ L mol}^{-1}$
- $b = 4.390 \text{ L atm mol}^{-1}$

$$\text{Difference} = (1.223 - 1.215) = 0.008 \text{ atm}$$

Notice that there isn't a large deviation between the two values. But some gases may cause the difference to be more noticeable. This is especially noticeable when the temperatures are low and the pressures are high. There exist cases when these equations FAIL and other equations are developed known as **virial** equations.

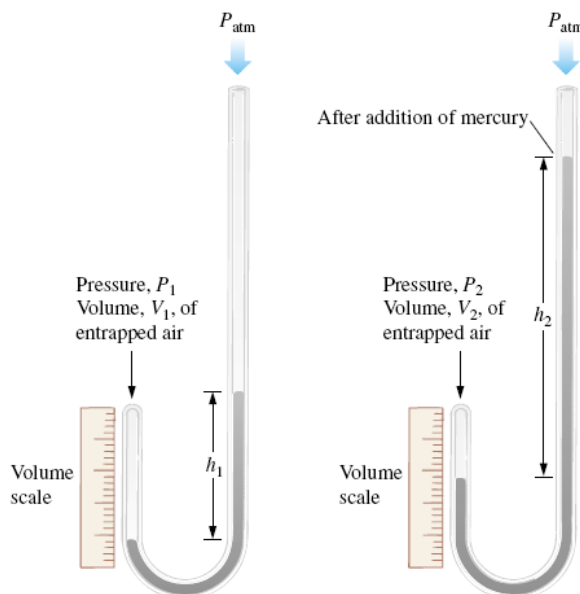
## 5.2. DIFFERENCES BETWEEN REAL AND IDEAL GASES

### 5.3. THE GAS LAWS

#### 5.3.1. BOYLE'S LAW

During the seventeenth century, Robert Boyle (1627 – 1691) carried out early experiments on the behaviour of gases.

##### 5.3.1.1. THE EXPERIMENT



**Figure 2** – A representation of Boyle's experiment. A sample of air is trapped in a tube in such a way that the pressure on the air can be changed and the volume of the air measured.  $P_{atm}$  is the atmospheric pressure, measured with a barometer.  $P_1 = h_1 + P_{atm}$ ,  $P_2 = h_2 + P_{atm}$ . (Whitten et al., 2004)

A sample of gas was trapped in a U – tube and allowed to come to constant temperature. Then its volume and the difference in the heights of the two mercury columns were recorded. This difference in height plus the pressure of the atmosphere represents the pressure on the gas. Addition of more mercury to the tube increases the pressure by changing the height of the mercury column. As a result, the gas volume decreases.

Boyle showed that for a given sample of gas at constant temperature, the product of pressure and volume,  $P \times V$ , was always the same number.

At a given temperature, the product of pressure and volume of a definite mass of gas is constant.

$$PV = k (\text{constant } n, T)$$

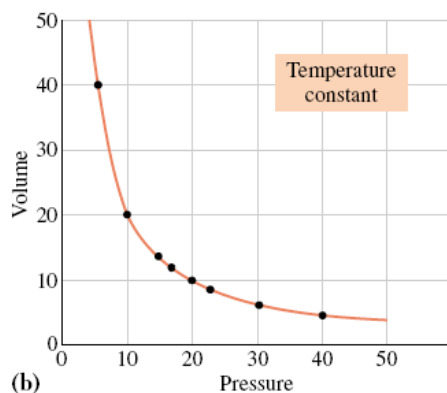
This relationship is Boyle's law. The value  $k$  depends on the amount (number of moles,  $n$ ) of gas present and on the temperature. Units for  $k$  are determined by the units used to express the volume ( $V$ ) and the pressure ( $P$ ).

### 5.3.1.2. GRAPHICAL TREATMENT

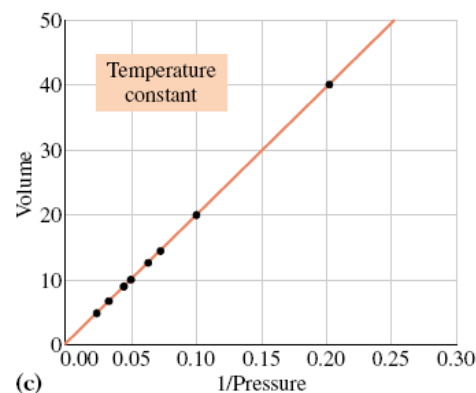
When the volume of a gas is plotted against its pressure at constant temperature, the resulting curve is one branch of a hyperbola. When the volume,  $V$ , is plotted against the reciprocal of pressure,  $1/P$ , a straight line results as can be seen.

$P$	$V$	$P \times V$	$1/P$
5.0	40.0	200	0.20
10.0	20.0	200	0.10
15.0	13.3	200	0.0667
17.0	11.8	201	0.0588
20.0	10.0	200	0.0500
22.0	9.10	200	0.0455
30.0	6.70	201	0.0333
40.0	5.00	200	0.0250

(a)



(b)



(c)

**Figure 3** – (a) Some typical data from an experiment such as that shown in **Figure 3**. Measured values of  $P$  and  $V$  are presented in the first two columns, on an arbitrary scale. (b, c) Graphical representations of Boyle's Law, using the data of part (a). (b)  $V$  versus  $P$ . (c)  $V$  versus  $1/P$ . (Whitten et al., 2004)

In 1662, Boyle summarised the results of his experiments on various samples of gases in an alternative statement of Boyle's Law:

At constant temperature, the volume,  $V$ , occupied by a definite mass of a gas is inversely proportional to the applied pressure,  $P$ .

$$V \propto \frac{1}{P} \quad \text{or} \quad V = k \left( \frac{1}{P} \right) \quad (\text{constant } n, T)$$

At normal temperatures and pressure, most gases obey Boyle's Law rather well. This is known as **ideal behaviour**.

Consider a fixed mass of gas at constant temperature, but at two different conditions of pressure and volume. For the first condition,

$$P_1 V_1 = k \quad (\text{constant } n, T)$$

And for the second condition:

$$P_2 V_2 = k \quad (\text{constant } n, T)$$

Because the right hand sides of these equations are the same, the left hand sides must be equal, or:

$$P_1V_1 = P_2V_2$$

(for a given amount of gas at constant temperature)

This form of Boyle's Law is useful for calculations involving pressure and volume changes.

### 5.3.1.3. SAMPLE PROBLEMS

#### Problem

A sample of gas occupies 12 L under a pressure of 1.2 atm. What would its volume be if the pressure were increased to 2.4 atm?

#### Solution

- $V_1 = 12 \text{ L}$
- $V_2 = ?$
- $P_1 = 1.2 \text{ atm}$
- $P_2 = 2.4 \text{ atm}$

Solving Boyle's Law,  $P_1V_1 = P_2V_2$  for  $V_2$  and substituting gives:

$$V_2 = \frac{P_1V_1}{P_2} = \frac{(1.2 \text{ atm})(12 \text{ L})}{2.4 \text{ atm}} = 6.0 \text{ L}$$

#### Problem

A sample of oxygen occupies 10.0 L under a pressure of 790 torr (105 kPa). At what pressure would it occupy 13.4 L if the temperature did not change?

#### Solution

- $V_1 = 10 \text{ L}$
- $V_2 = 13.4 \text{ L}$
- $P_1 = 790 \text{ Torr}$
- $P_2 = ?$

Solving Boyle's Law,  $P_1V_1 = P_2V_2$  for  $P_2$  and substituting gives:

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(790 \text{ Torr})(10.0 \text{ L})}{13.4 \text{ L}} = 590 \text{ Torr}$$

### 5.3.2. CHARLES LAW

Charles's law (also known as the law of volumes) is an experimental gas law which describes how gases tend to expand when heated. It was first published by French natural philosopher Joseph Louis Gay – Lussac in 1802, although he credits the discovery to unpublished work from the 1780s by Jacques Charles. The law was independently discovered by British natural philosopher John Dalton by 1801, although Dalton's description was less thorough than Gay – Lussac's. The basic principles had already been described a century earlier by Guillaume Amontons.

Whatever the priority of the discovery, Gay – Lussac was the first to demonstrate that the law applied generally to all gases, and also to the vapours of volatile liquids if the temperature was more than a few degrees above the boiling point. His statement of the law can be expressed mathematically as:

$$V_{100} - V_0 = kV_0$$

**Where**

- $V_{100}$  is the volume occupied by a given sample of gas at 100 °C;
- $V_0$  is the volume occupied by the same sample of gas at 0 °C;
- $k$  is a constant which is the same for all gases at constant pressure.

Gay-Lussac's value for  $k$  was  $\frac{1}{2.6666}$ , remarkably close to the present-day value of  $\frac{1}{2.7315}$ .

A modern statement of Charles's law is:

At constant pressure, the volume of a given mass of an ideal gas increases or decreases by the same factor as its temperature on the absolute temperature scale (i.e. the gas expands as the temperature increases). This can be written as:

$$V \propto T$$

**Where**

- $V$  is the volume of the gas;
- $T$  is the absolute temperature.

The law can also be usefully expressed as follows:

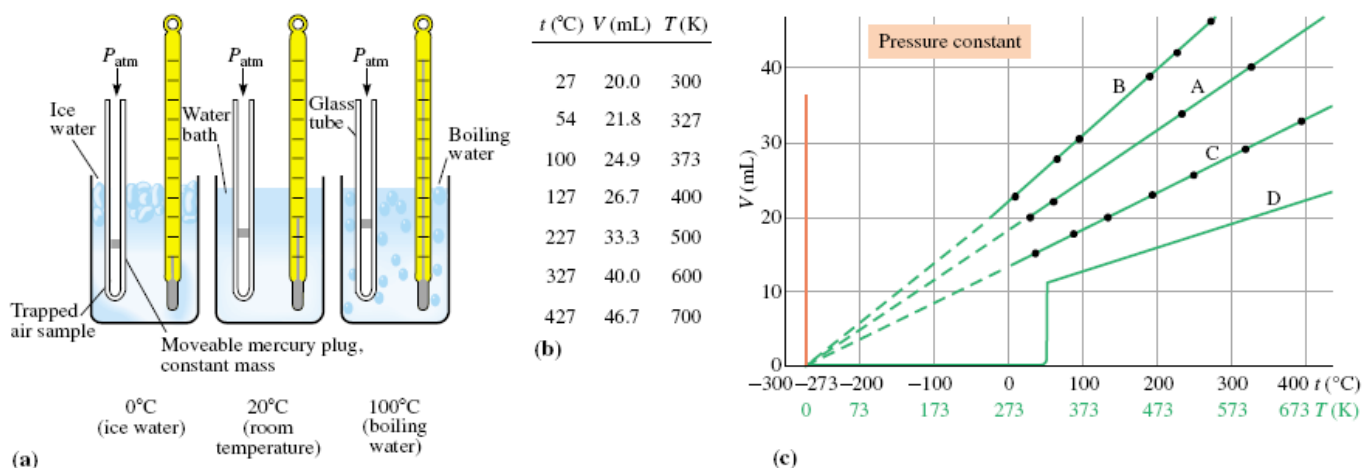
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$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	<b>OR</b>	$\frac{V_2}{V_1} = \frac{T_2}{T_1}$	<b>OR</b>	$V_1 T_2 = V_2 T_1$
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The equation shows that, as absolute temperature increases, the volume of the gas also increases in proportion.

### 5.3.2.1. GRAPHICAL REPRESENTATIONS



**Figure 4** - An experiment showing that the volume of an ideal gas increases as the temperature is increased at constant pressure. (a) A mercury plug of constant weight, plus atmospheric pressure, maintains a constant pressure on the trapped air. (b) Some representative volume–temperature data at constant pressure. The relationship becomes clear when  $t$  (°C) is converted to  $T$  (K) by adding 273°C. (c) A graph in which volume is plotted versus temperature on two different scales. Lines A, B, and C represent the same mass of the same ideal gas at different pressures. Line A represents the data tabulated in part (b). Graph D shows the behaviour of a gas that condenses to form a liquid (in this case, at 50°C) as it is cooled. (Whitten et al., 2004)

### 5.3.2.2. CALCULATIONS

#### Problem

A sample of gas at 101.3kPa had a volume of 1.2L at 100°C. What would its volume be at 0°C at the same pressure?

#### Solution

- $V_i = 1.2\text{L}$
- $V_f = ?$
- $T_i = 100^\circ\text{C} = 100 + 273 = 373\text{K}$
- $T_f = 0^\circ\text{C} = 0 + 273 = 273\text{K}$

$$\frac{1.2}{373} = \frac{V_f}{273}$$

$$\rightarrow 3.22 \times 10^{-3} = \frac{V_f}{273}$$

$$\rightarrow V_f = 3.22 \times 10^{-3} \times 273 = 0.88\text{L (880mL)}$$

#### Problem

A balloon had a volume of 75L at 25°C. To what does the temperature need to be raised in order for the balloon to have a volume of 100L at the same pressure?

**Solution**

- $V_i = 75\text{L}$
- $V_f = 100\text{L}$
- $T_i = 25^\circ\text{C} = 25 + 273 = 298\text{K}$
- $T_f = ? (\text{K})$

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

**Substituting values into equation:**

$$\begin{aligned} \frac{75}{298} &= \frac{100}{T_f} \\ 0.2517 &= \frac{100}{T_f} \\ T_f &= \frac{100}{0.2517} = 397\text{K} = 124^\circ\text{C} \end{aligned}$$

### 5.3.3. THE IDEAL GAS EQUATION

The **ideal gas law** is the equation of state of a hypothetical ideal gas. It is a good approximation to the behaviour of many gases under many conditions, although it has several limitations. It was first stated by Émile Clapeyron in 1834 as a combination of Boyle's law and Charles's law. It can also be derived from kinetic theory, as was achieved (apparently independently) by August Krönig in 1856 and Rudolf Clausius in 1857.

The state of an amount of gas is determined by its pressure, volume, and temperature. The modern form of the equation is:

$$pV = nRT$$

Where

- $p$  is the absolute pressure of the gas;
- $V$  is the volume;
- $n$  is the amount of substance (mol);
- $R$  is the gas constant;
- $T$  is the absolute temperature.

In SI units,  $p$  is measured in pascals;  $V$  in cubic metres;  $n$  in moles; and  $T$  in kelvin.  $R$  has the value  $8.314472 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  in SI units.

**Since it neglects both molecular size and intermolecular attractions, the ideal gas law is most accurate for monatomic gases at high temperatures and low pressures.** The neglect of molecular size becomes less important for lower densities, i.e. for larger volumes at lower pressures, because the average distance between adjacent molecules

becomes much larger than the molecular size. The relative importance of intermolecular attractions diminishes with increasing thermal kinetic energy i.e., with increasing temperatures. More detailed equations (usually referred to as equations of state) such as the van der Waals equation, allow deviations from ideality caused by molecular size and intermolecular forces to be taken into account. This was described earlier.

### 5.3.4. CALCULATIONS

#### Problem

What volume is needed to store 0.050 moles of helium gas at 202.6kPa and 400K?

#### Solution

$$PV = nRT$$

- $P = 202.6 \text{ kPa}$
- $n = 0.050 \text{ mol}$
- $T = 400\text{K}$
- $V = ? \text{ L}$
- $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\begin{aligned} 202.6 \times V &= 0.050 \times 8.314 \times 400 \\ 202.6 \times V &= 166.28 \\ \rightarrow V &= \frac{166.28}{202.6} \\ \rightarrow V &= 0.821 \text{ L (821 mL)} \end{aligned}$$

#### Problem

What pressure will be exerted by 20.16g hydrogen gas in a 7.5L cylinder at 20°C?

#### Solution

$$PV = nRT$$

- $P = ? \text{ kPa}$
- $V = 7.5\text{L}$
- $n = ?$
- $T = 20^\circ = 20 + 273 = 293\text{K}$
- $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

**Notice that we have two quantities that are unknown, but we have the mass of the gas, so we can find the number of moles as follows:**

- $\text{mass} = 20.16\text{g}$
- $\text{molecular mass (H}_2) = 2 \times 1.008 = 2.016\text{g/mol}$

$$n = \frac{\text{mass}}{\text{molecular mass}}$$

$$\rightarrow n = \frac{20.16}{2.016} = 10 \text{ mol}$$

So now we have the number of moles and we can proceed to find the pressure:

$$P \times 7.5 = 10 \times 8.314 \times 293$$

$$P \times 7.5 = 24360.02$$

$$P = \frac{24360.02}{7.5} = 3248 \text{ kPa}$$

### Problem

A 50L cylinder is filled with argon gas to a pressure of 10130.0kPa at 30°C. How many moles of argon gas are in the cylinder?

### Solution

$$PV = nRT$$

$$P = 10130.0\text{kPa}$$

$$V = 50\text{L}$$

$$n = ? \text{ mol}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 30^\circ\text{C} = 30 + 273 = 303\text{K}$$

$$10130.0 \text{ (kPa)} \times 50\text{(L)} = n \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 303 \text{ K}$$

$$506500 = n \times 2519.142$$

$$\rightarrow n = \frac{506500}{2519.142} = 201.1 \text{ mol}$$

### Problem

To what temperature does a 250mL cylinder containing 0.40g helium gas need to be cooled in order for the pressure to be 253.25kPa?

### Solution

$$PV = nRT$$

- $P = 253.25\text{kPa}$
- $V = 250\text{mL} = 250/1000 = 0.250\text{L}$
- $n = ?$
- $R = 8.314 \text{ J K mol}^{-1}$
- $T = ? \text{ K}$

$$n = \frac{\text{mass}}{\text{molecular mass}}$$

- $\text{mass} = 0.40\text{g}$

- molecular mass (He) = 4.003g/mol  
 $n = 0.40 \div 4.003 = 0.10\text{mol}$

$$253.25 \times 0.250 = 0.10 \times 8.314 \times T$$

$$63.3125 = 0.8314 \times T$$

$$\rightarrow T = \frac{63.3125}{0.8314} = 76.15\text{K}$$

## 5.4. EXPLANATIONS

### 5.4.1. THE LIQUID STATE

Liquid is one of the three primary states of matter, with the others being solid and gas. A liquid is a fluid. Unlike a solid, the molecules in a liquid have a much greater freedom to move. The forces that bind the molecules together in a solid are only temporary in a liquid, allowing a liquid to flow while a solid remains rigid.

A liquid, like a gas, displays the properties of a fluid. A liquid can flow, assume the shape of a container, and, if placed in a sealed container, will distribute applied pressure evenly to every surface in the container. Unlike a gas, a liquid may not always mix readily with another liquid, will not always fill every space in the container, forming its own surface, and will not compress significantly, except under extremely high pressures. These properties make a liquid suitable for applications such as hydraulics.

Liquid particles are bound firmly but not rigidly. They are able to move around one another freely, resulting in a limited degree of particle mobility. As the temperature increases, the increased vibrations of the molecules cause distances between the molecules to increase. When a liquid reaches its boiling point, the cohesive forces which bind the molecules closely together break and the liquid changes to its gaseous state (unless superheating occurs). If the temperature is decreased, the distances between the molecules become smaller. When the liquid reaches its freezing point the molecules will usually lock into a very specific order, called crystallizing, and the bonds between them become more rigid, changing the liquid into its solid state (unless supercooling occurs).

### 5.4.2. MELTING & VAPOURIZATION

#### 5.4.2.1. MELTING AND FREEZING

If energy is supplied by heating a solid, the heat energy causes stronger vibrations until the particles eventually have enough energy to break away from the solid arrangement to form a liquid. The heat energy required to convert 1 mole of solid into a liquid at its melting point is called the *enthalpy of fusion*.

When a liquid freezes, the reverse happens. At some temperature, the motion of the particles is slow enough for the forces of attraction to be able to hold the particles as a solid. As the new bonds are formed, heat energy is evolved.

### 5.4.2.2. BOILING AND CONDENSING

If more heat energy is supplied, the particles eventually move fast enough to break all the attractions between them, and the liquid boils. The heat energy required to convert 1 mole of liquid into a gas at its boiling point is called the ***enthalpy of vaporisation***.

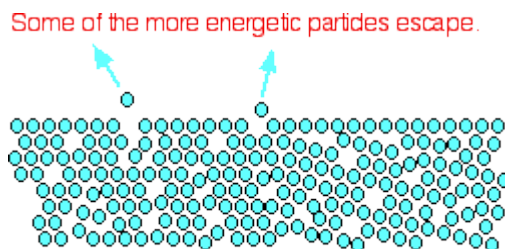
If the gas is cooled, at some temperature the gas particles will slow down enough for the attractions to become effective enough to condense it back into a liquid. Again, as those forces are re-established, heat energy is released.

### 5.4.2.3. THE EVAPORATION OF A LIQUID

The *average* energy of the particles in a liquid is governed by the temperature. The higher the temperature, the higher the average energy. But within that average, some particles have energies higher than the average, and others have energies lower than the average.

Some of the more energetic particles on the surface of the liquid can be moving fast enough to escape from the attractive forces holding the liquid together. They evaporate.

The diagram shows a small region of a liquid near its surface.



Notice that evaporation only takes place on the surface of the liquid. That's quite different from boiling which happens when there is enough energy to disrupt the attractive forces throughout the liquid. That's why, if you look at boiling water, you see bubbles of gas being formed all the way through the liquid.

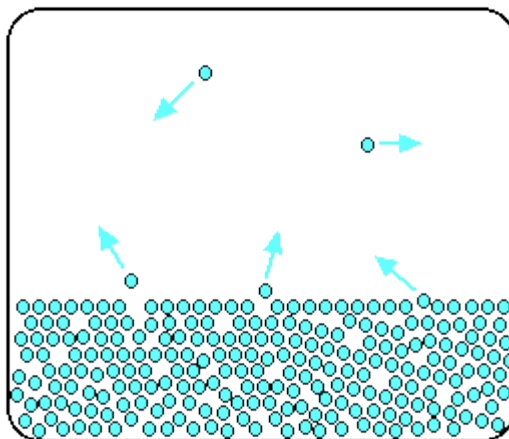
If you look at water which is just evaporating in the sun, you don't see any bubbles. Water molecules are simply breaking away from the surface layer.

Eventually, the water will all evaporate in this way. The energy which is lost as the particles evaporate is replaced from the surroundings. As the molecules in the water jostle with each other, new molecules will gain enough energy to escape from the surface.

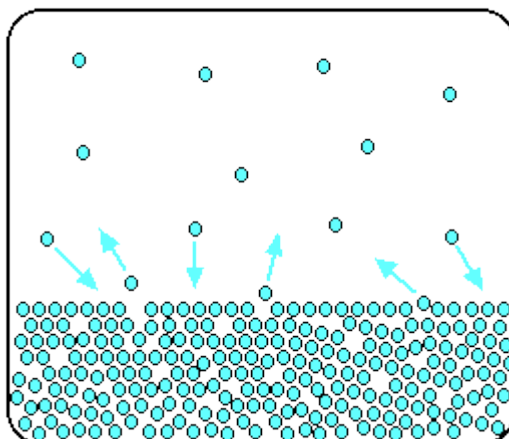
### 5.4.2.4. A CLOSED CONTAINER

Now imagine what happens if the liquid is in a closed container. Common sense tells you that water in a sealed bottle doesn't seem to evaporate - or at least, it doesn't disappear over time.

But there is constant evaporation from the surface. Particles continue to break away from the surface of the liquid - but this time they are trapped in the space above the liquid.



As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and be trapped there. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it.



In this equilibrium, there will be a fixed number of the gaseous particles in the space above the liquid.

When these particles hit the walls of the container, they exert a pressure. This pressure is called the **saturated vapour pressure** (also known as **saturation vapour pressure**) of the liquid.

### **SUBLIMATION**

Solids can also lose particles from their surface to form a vapour, except that in this case we call the effect **sublimation** rather than evaporation. Sublimation is the direct change from solid to vapour (or vice versa) without going through the liquid stage.

In most cases, at ordinary temperatures, the saturated vapour pressures of solids range from low to very, very, very low. The forces of attraction in many solids are too high to allow much loss of particles from the surface.

However, there are some which do easily form vapours. For example, naphthalene (used in old-fashioned "moth balls" to deter clothes moths) has quite a strong smell. Molecules must be breaking away from the surface as a vapour, because otherwise you wouldn't be able to smell it.

Another fairly common example (discussed in detail elsewhere on the site) is solid carbon dioxide - "dry ice". This never forms a liquid at atmospheric pressure and always converts directly from solid to vapour. That's why it is known as dry ice.

## 5.5. REFERENCES

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