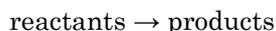


Topic 7 – Equilibrium (Standard Level)

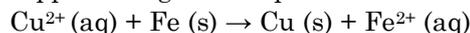
Overview

So far we have made the assumption that all chemical reactions go to completion. We have said that the reactants written on the left of the arrow in the chemical equation change completely into the products written on the right of the arrow:



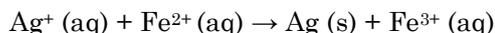
We have assumed that all reactions continue from left to right until one or more of the reactants are exhausted and there is none remaining to react. We used this assumption in Topic 1 to calculate the expected amount of a product formed in a reaction when given the amount of reactants initially mixed together. Many reactions, however, do not go entirely to completion. The yield of the reaction may not be 100%. At the apparent end of the reaction there is a mixture of reactants and products.

Let's look at a couple of simple test tube reactions. When iron filings are stirred into a bright blue aqueous solution of copper(II) sulfate, the colour of the solution changes quite rapidly to pale green. The original blue colour of the solution was due to aqueous copper(II) ions, $\text{Cu}^{2+}(\text{aq})$. During the reaction, the $\text{Cu}^{2+}(\text{aq})$ ions are displaced from solution and replaced by $\text{Fe}^{2+}(\text{aq})$ ions, which are pale green in colour. Orange copper solid is deposited at the bottom of the beaker. The reaction appears to go to completion in the direction of the arrow:

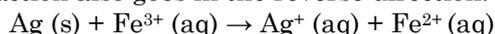


This reaction only goes in one direction. We say the reaction is irreversible. It is not possible to mix the products (solid copper and a solution of iron(II) ions) together in test tube and reform the reactants.

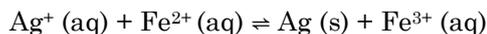
A similar displacement reaction occurs when a solution of silver ions is mixed with a solution of iron(II) ions. In this reaction, silver is deposited at the bottom of the test tube. However, the mass of silver deposited is not as much as that predicted from the amount of silver ions in the original solution. The reaction:



appears not to go to completion. There is a mixture of all four species (the reactants $\text{Ag}^{+}(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$, and the products $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$) at the “end” of the reaction. But is it really the end of the reaction? It certainly *appears* that way. The amount of silver at the bottom of the beaker and the colour of the solution due to the dissolved ions does not change any further. Now here's an interesting thing: if you start with the products, that is, with solid silver and a solution of iron(III) ions, and mix them together, a similar mixture of the four substances will be formed. The reaction also goes in the reverse direction:



This reaction is **reversible**. Many chemical reactions show the ability, under the right conditions, to proceed in both directions. At the apparent end of the reaction (though in fact this reaction has no real “end”, as we will find out later) there is an intermediate position or **equilibrium** in which both reactants and products are present. The chemical equation for a reversible change like this no longer uses a single \rightarrow arrow to represent a unidirectional change from reactants to products. Instead, a special \rightleftharpoons sign is used to indicate that the change can occur in both directions:



It is not only chemical changes that are reversible. Under the right conditions, physical changes can be reversible, and this is where we will start our discussion of equilibrium.

The topic of equilibrium at standard level asks you to recognise that some chemical and physical changes do not go to completion. There is a mixture of substances at the end of the change. This mixture can be approached from either side: the “reactants” side or the “products” side. We introduce a way of quantifying the composition of the mixture at equilibrium, but there are no calculations to do at standard level. We then look at how the composition of the mixture at equilibrium varies when we change external factors like the temperature and the concentrations of species present. Not only is this interesting, but it is also extremely important. We shall see how we can adjust the composition of this **equilibrium mixture** in our favour, and we will apply these ideas to two very important chemical reactions in industry.

7.1 Dynamic Equilibrium

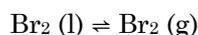
Equilibria in Physical Processes

Bromine is one of the two elements that is a liquid at room temperature. It is a volatile dark brown liquid. When a small volume of bromine liquid is added to a gas jar, some of the faster moving Br₂ molecules near the surface escape from the liquid. This is the process of vaporization. An orange vapour forms above the liquid due to gaseous bromine molecules. Molecules in the vapour can move around freely, bouncing into each other and off the sides of the gas jar. Collisions between the molecules in the vapour and the sides of the gas jar create a pressure on the inside of the container. This is called the vapour pressure. If a fast moving molecule in the vapour collides with the surface of the liquid, it can be captured by the attractive van der Waals' forces of the more closely packed molecules in the liquid phase. The process of condensation describes particles entering the liquid phases from the gas phase.

Study Hint:

The terms “vapour” and “gas” are often used interchangeably. Strictly speaking, a vapour is a gas that can be turned into a liquid by compressing it alone (and without having to cool it at the same time). Above a critical temperature, a gas will not form a liquid no matter how much it is compressed. The gas is not a vapour above this critical temperature.

If we keep a lid on the gas jar and maintain a constant temperature, then after a time the intensity of the orange colour of the bromine vapour trapped inside the gas jar does not change any further: the vapour does not get lighter or darker in colour. This does not mean that the opposing processes of vaporization and condensation have stopped. Vaporization and condensation continue but they continue *at the same rate*. As fast as Br₂ molecules escape from the liquid into the gas phase, other molecules rejoin the liquid from the gas phase. This situation is shown in Figure 7.1 (a). The system has achieved a point of balance. We say that a **state of equilibrium** has been reached:

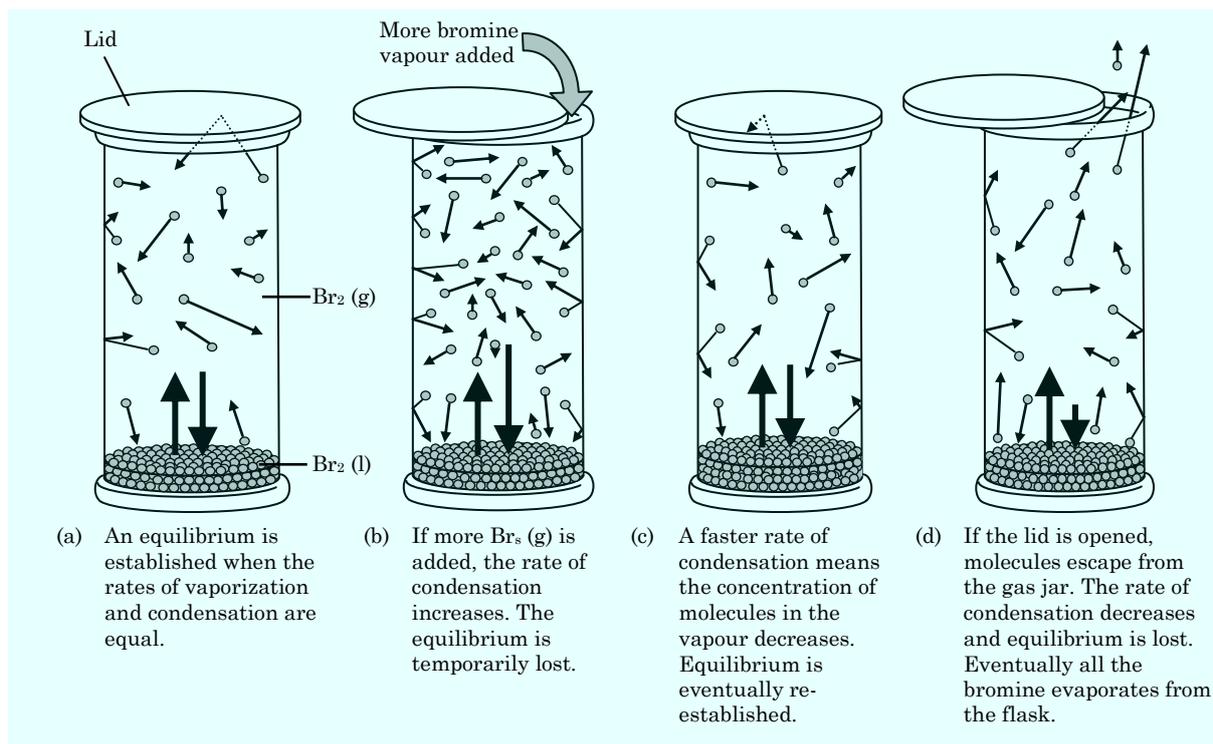


At equilibrium, the concentration of Br₂ molecules in the vapour remains constant. Now, it is much easier to measure the pressure exerted by the vapour on the walls of its container than its concentration. At the point where the processes of vaporization and condensation are balanced, the pressure of the vapour above the liquid is called the **saturated vapour pressure**. The saturated vapour pressure is the maximum pressure exerted by the vapour at a given temperature. Providing the temperature remains the same, the saturated vapour pressure is constant when the system is in equilibrium.

Now imagine that the lid on the gas jar is lifted temporarily and more Br₂ vapour is added (Figure 7.1 (b)). As there are now more molecules in the gas phase, more will collide with the walls of the gas jar and with the surface of the liquid bromine. The rate of condensation is now greater than the rate of vaporization. The state of equilibrium has been lost. But equilibrium situations, given the opportunity, have a habit of re-forming. An increase in the rate of condensation means that there are soon fewer Br₂ (g) molecules in the vapour. Eventually, the rate of condensation decreases and once again matches the rate of vaporization. The equilibrium is re-established, as shown in Figure 7.1 (c).

What happens if the lid on the gas jar is removed permanently? Now Br₂ molecules in the vapour phase can escape from the flask. Molecules escaping from the flask are replaced by more evaporating from the liquid. The equilibrium situation is lost. Eventually, all the bromine will evaporate from the gas jar to the surroundings. The equilibrium state cannot re-form if the lid is left off (Figure 7.1 (d)). Equilibrium can only be formed in a **closed system** where there is no exchange of particles between the system and the surroundings. Energy can be exchanged but the gain or loss of particles disturbs the equilibrium or prevents the equilibrium from forming at all.

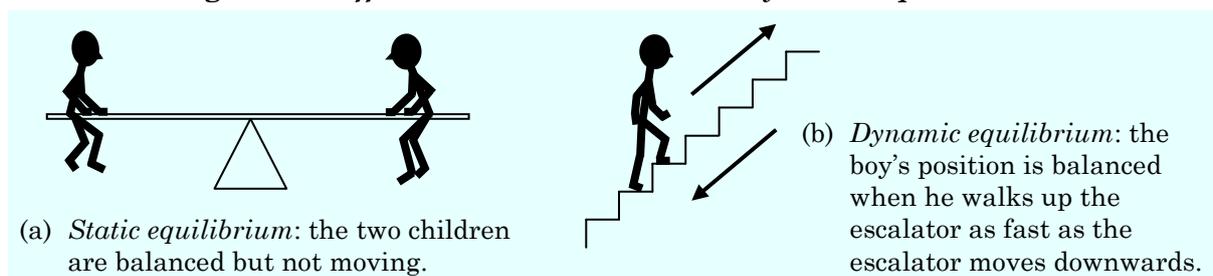
The nature of dynamic equilibrium and the need for a closed system is nicely illustrated in <http://www.youtube.com/watch?v=JsoawKguU6A>.

Figure 7.1 Phase Equilibrium Between a Liquid and a Vapour


So a state of equilibrium implies a state of balance. When the bromine liquid and vapour are in equilibrium with one another, the intensity of the orange colour of the vapour stays the same. It is tempting to think that at this point of balance everything has stopped in order to “keep the balance”. Certainly, macroscopic properties, things like concentration or pressure that we can measure in the laboratory, do remain constant at equilibrium. However, microscopic processes, in other words, what is actually happening to the particles – reacting or changing state – continue at equilibrium. Chemical equilibrium is a **dynamic equilibrium**. A balance is achieved because the forward and reverse processes are occurring at the same rate.

A dynamic equilibrium is established when the rates of two opposing changes are balanced

The following analogy might also help you clarify the difference between a dynamic and static equilibrium. Imagine two children sitting at opposite ends of a see-saw (Figure 7.2 (a)). If they adjust their positions, the see-saw can reach a state of equilibrium; the children can balance each other. This is a static equilibrium. If one of the children moves, the balance is lost. Now imagine a boy walking up a “down” escalator (Figure 7.2 (b)). If the boy walks up the escalator at the same speed as the escalator is moving down, then his position does not change. The boy makes no progress upwards. He is in a position of equilibrium. This time, however, it is a dynamic equilibrium. If one of the processes stops (either the boy stops walking or someone switches off the escalator), the equilibrium is lost.

Figure 7.2 Difference between Static and Dynamic Equilibrium


Topic 7 - Core

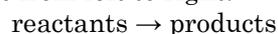
Let's summarise what we have seen so far:

- An equilibrium is established when the rate of two opposing processes balance. This is called a dynamic equilibrium.
- At equilibrium, macroscopic properties like amounts, concentrations or pressures of all species involved remain constant; however microscopic processes still occur.
- A dynamic equilibrium can be approached from either side. Providing external conditions like temperature and pressure are kept constant, an equilibrium mixture of species will be formed.
- Equilibrium can only be established in a closed system in which there is no transfer of materials between system and surroundings.

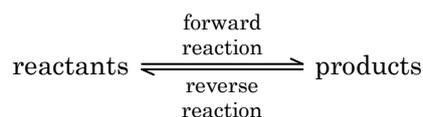
We can now apply these findings to chemical reactions.

Equilibria in Chemical Processes

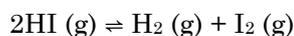
First, let's start with the terminology used to describe equilibrium reactions. In irreversible reactions, we call the species that we start with "the reactants" and the species that we finish with "the products". The reaction goes from left to right:



But what about reversible reactions that go in both directions? We still call the species written on the left of the \rightleftharpoons arrow the reactants and those on the right the products, even though the reaction occurs in both directions. In the IB syllabus (and therefore in exams) the reaction from right to left is called the reverse reaction; in some books it is called the backward reaction:



Here's a real example of a chemical equilibrium. Hydrogen iodide, HI, dissociates into its elements, hydrogen and iodine. However, the dissociation is incomplete even at high temperatures. At any given temperature, there is a mixture of hydrogen, iodine and undissociated hydrogen iodide:

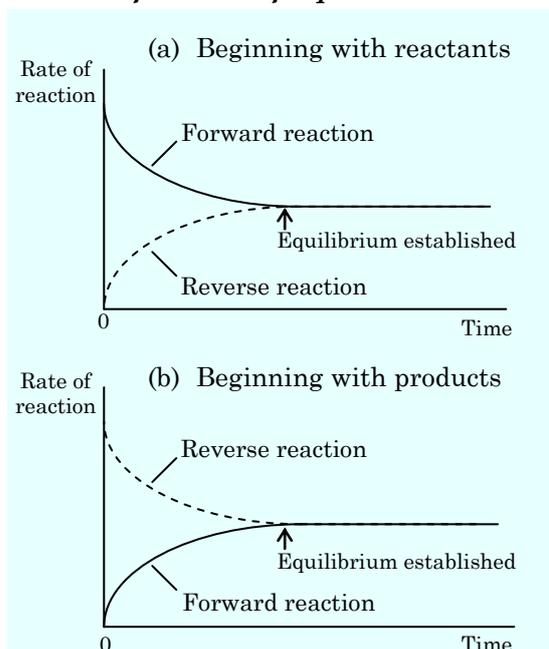


The mixture forms because as HI dissociates in the forward reaction, H_2 and I_2 recombine together to re-form HI in the opposite, reverse, direction. **At equilibrium, the rates of the forward and reverse reactions are equal.**

How do the rates of the forward and reverse reaction change with time in a reversible reaction? Well, if pure HI is introduced into a closed container, the rate of the forward reaction is initially very high as there is a lot of HI. The rate of the reverse reaction is initially zero as no products, H_2 and I_2 , exist (Figure 7.3 (a)). As more and more of the HI dissociates, the rate of the forward reaction slows as there is less HI remaining. The rate of the reverse reaction increases because the dissociation of HI forms more H_2 and I_2 that can react with each other. Finally, after a certain time interval after the introduction of the HI into the container, a state of equilibrium is established. The time taken for the equilibrium to be established depends on factors such as the rates of the individual reactions, the temperature of the mixture, the presence of catalysts and, for gaseous reactions, the pressure.

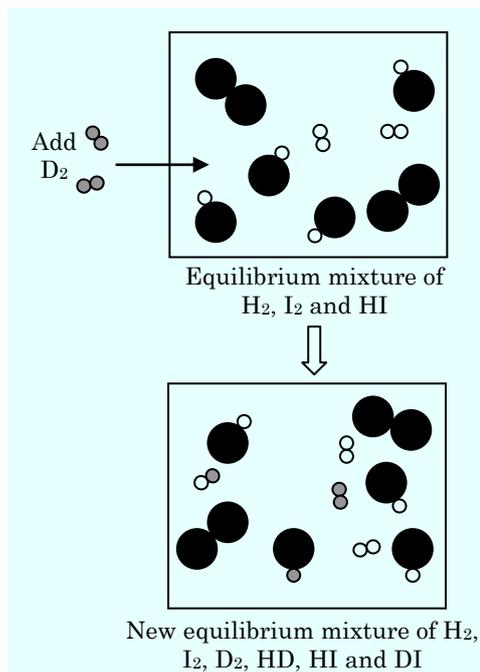
The analogous situation occurs when we start with products only, in other words, starting with H_2 and I_2 . Initially, the reverse reaction is very

Figure 7.3 Rates of Forward and Reverse Reactions and the Formation of a State of Equilibrium



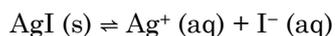
fast and there is no forward reaction (Figure 7.3 (b)). Eventually, the same state of equilibrium is reached, at which point the rates of forward and reverse reactions are matched.

What physical evidence is there that the forward and reverse reactions continue at equilibrium so that we have a dynamic not a static equilibrium? Macroscopic properties are constant and it appears that the situation is stationary after equilibrium has been established. One way is to introduce different atoms into the equilibrium mixture. In our example of the dissociation of HI, we could add some deuterium. Deuterium is one of the isotopes of hydrogen. An atom of deuterium (symbol ^2H , or sometimes simply written as D) has an extra neutron in the nucleus compared to a hydrogen atom (^1H) but is chemically identical. Let's say we add some deuterium molecules, D_2 , to an equilibrium mixture of HI, H_2 and I_2 . After a while we would find that as well as HI, we have some DI in the equilibrium mixture. We would also find some HD in the mixture. This is made from the exchange of hydrogen and deuterium atoms in H_2 molecules. Deuterium atoms have become integrated into the equilibrium mixture. This can only happen if the forward and reverse reactions are continuing in the equilibrium mixture.

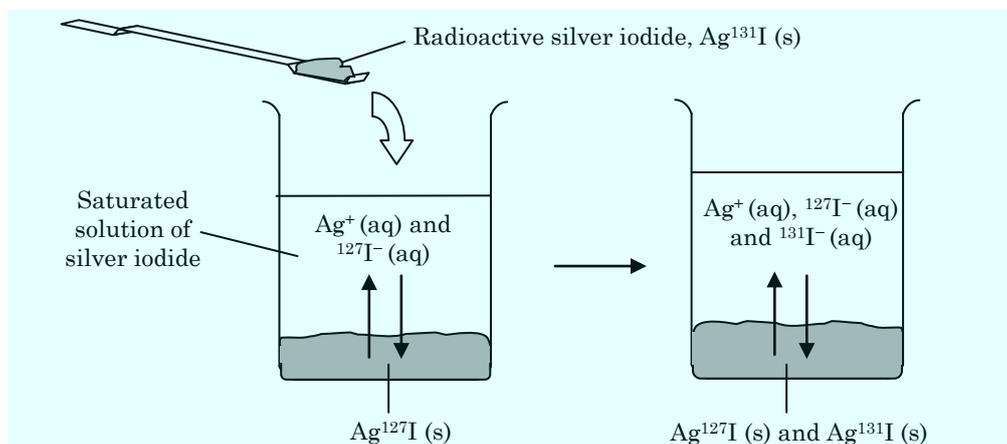


In the same way, if some deuterium iodide, DI, is added to an equilibrium mixture of HI, H_2 and I_2 , a new equilibrium mixture of DI, HI, H_2 , HD and a little D_2 will be formed.

The more sceptical of you might still not be convinced. You might argue that the addition of the D_2 temporarily disturbs the equilibrium, restarting the forward and reverse reactions before they stop again at a new equilibrium. The next example should convince you of the dynamic nature of chemical equilibria. Imagine you are given a saturated solution of silver iodide, AgI (aq). A saturated solution contains the maximum amount of dissolved solute at a given temperature; no more AgI can dissolve in the solution. If more solid AgI is now added to the saturated solution, an equilibrium state is established between the solid silver iodide and the silver and iodide ions in the solution:

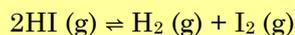


We can use the process of **radioactive labelling** to test the dynamic nature of the equilibrium. Naturally occurring iodine exists as the non-radioactive isotope ^{127}I . ^{131}I is a radioactive isotope of iodine that can be made artificially. More solid silver iodide is added to the equilibrium mixture, but this time the extra silver iodide contains radioactive iodine, that is, Ag^{131}I as opposed to Ag^{127}I . Remember, no more silver iodide can dissolve in the saturated solution. Yet if the new mixture is left to stand for a while and then filtered, the filtered solution is found to be radioactive. This can only happen if the two opposing process (left to right and right to left in the equilibrium equation) continue at equilibrium.



Study Hint:

A common misconception of students is thinking that, because there is a balance between the rates of forward and reverse reactions at equilibrium, the total concentrations of reactants and the products at equilibrium must be the same (or “balanced”) as well. This is almost always not the case. The relative amounts of reactants and products in the equilibrium mixture depends on the initial amounts of substances present and on how much the equilibrium “favours” one side or another. This is referred to as the position of the equilibrium. We shall look at this in the next section. For example, in the dissociation of hydrogen iodide:



there is much more HI than H_2 and I_2 present in an equilibrium mixture at 450 °C. This does not mean that the forward reaction must be slower because there is more reactant HI present. Remember at equilibrium the forward and reverse reactions continue at the same speed.

We can work out what happens to the concentrations of reactants and products in the reaction mixture before and after equilibrium is established and display this in a graph. Let’s start with undissociated HI in a sealed container. The concentration of HI is initially high and there is no H_2 and I_2 present (Figure 7.4 (a)). As some of the HI dissociates, the concentrations of H_2 and I_2 increase. As equilibrium is established, the concentrations of HI, H_2 and I_2 reach constant values. Notice on Figure 7.4 (a) that the concentration of HI in the equilibrium mixture is higher than the concentrations of H_2 and I_2 ; this equilibrium favours the reactant at this particular temperature. Also note that the decrease in concentration of HI from its initial value to the equilibrium value is double the increase in concentration of H_2 and I_2 . This matches the coefficients in the balanced equation, which show that two moles of HI dissociate to form one mole each of H_2 and I_2 . The concentrations of H_2 and I_2 in this equilibrium mixture are the same because their initial concentrations were zero and they are formed in the same proportion when HI dissociates.

Figure 7.4 Concentrations of Reactant and Products in the Equilibrium
 $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ at Different Times

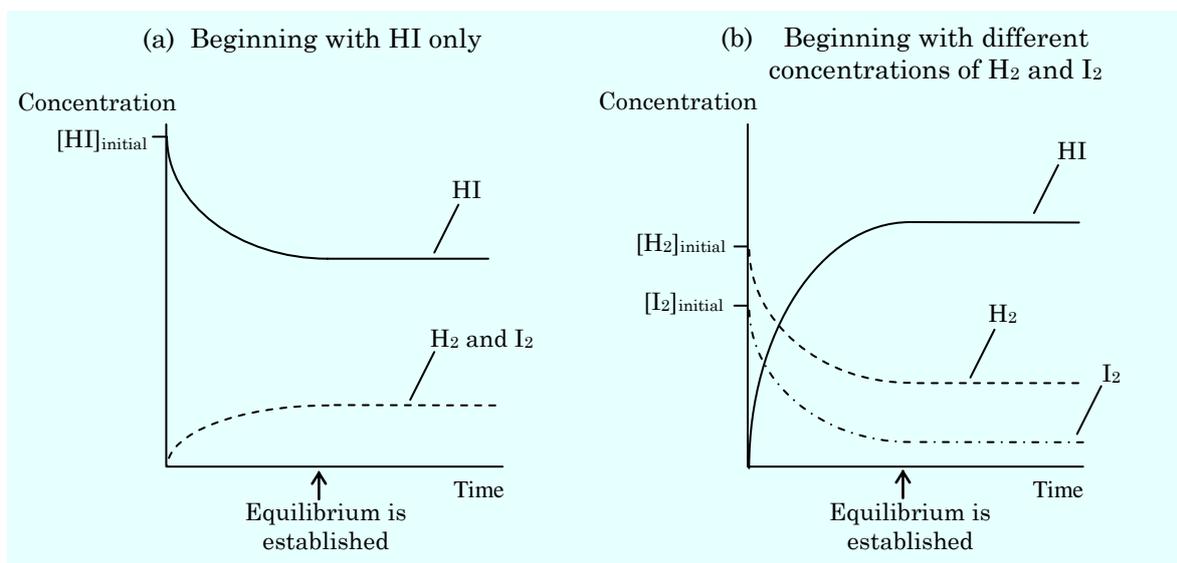


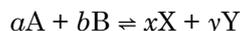
Figure 7.4 (b) shows what happens to the concentrations of all three molecules when we start with products only. In this particular case, the initial concentration of H_2 was higher than the initial concentration of I_2 . The concentrations of H_2 and I_2 decrease when they begin reacting together in the reverse reaction. The concentrations decrease by the same amount as they react in an equimolar (one to one) proportion to form two moles of HI. Again, there is more HI present in the equilibrium mixture than H_2 and I_2 even though there was none present at the start.

7.2 Position of Equilibrium

The Equilibrium Constant

We can see from Figure 7.4 that in the equilibrium between hydrogen iodide and its elements there is much more of the reactant HI than products H₂ and I₂ present in the equilibrium mixture at this test temperature. In the terminology of equilibrium, we say that “the equilibrium, 2HI (g) ⇌ H₂ (g) + I₂ (g), lies to the left”.

In general, we can say for the equilibrium

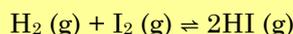


where A, B, X and Y are the symbols for the substances involved and *a*, *b*, *x* and *y* are the stoichiometric coefficients of each substance in the balanced chemical equation:

- If there are more reactants A and B than products X and Y in the equilibrium mixture, we say the equilibrium lies to the left;
- If there are more products X and Y in the equilibrium mixture, we say the equilibrium lies to the right.

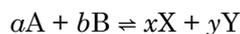
Study Hint:

Be careful using this terminology. It depends on which way round the equation for the reversible reaction is written. For example, the equilibrium reaction between HI, H₂ and I₂ could also be written as:



The equilibrium mixture would still contain more HI than H₂ and I₂ at the same temperature. Now we would say that the equilibrium lies to the right, as HI is a product when the equation is written this way round.

The equilibrium constant, *K_c*, gives us numerical values with which we can compare the relative proportions of reactants and products in the equilibrium mixture. The equilibrium constant is the ratio of the concentrations of the products to the reactants in the equilibrium mixture. We use square brackets to show concentrations in units of mol dm⁻³. For our general equilibrium reaction:



the equilibrium constant is:

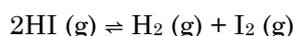
$$K_c = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Notice two things about this expression for *K_c*:

- it is “products over reactants”
- each concentration term is raised by a power equivalent to the coefficient for each substance in the balanced chemical equation.

It is important to point out that the equilibrium constant, *K_c*, uses the *equilibrium concentrations* of each of the substances, that is, the concentrations in the equilibrium mixture. To emphasise this point, in some books the concentration terms in the expression for *K_c* are written as []_{eqm} where “eqm” is shorthand for “equilibrium”. The equilibrium constant has no meaning until a state of equilibrium has been established in the reaction mixture.

Let's look at some real numbers. For the equilibrium:



the value of the equilibrium constant at 731 K (458 °C) is:

$$K_c = \frac{[H_2 (g)][I_2 (g)]}{[HI (g)]^2} = 0.021$$

In this equilibrium mixture at this temperature there is more reactant, HI, than products, H₂ and I₂. Remember that in the expression for *K_c* it is “products over reactants”, so the value for *K_c* where the equilibrium favours the reactants will be a fraction between 0 and 1.