

# EQUILIBRIUM

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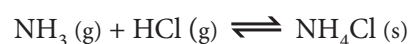
## 7.1 DYNAMIC EQUILIBRIUM

- 7.1.1 Outline the characteristics of chemical and physical systems in a state of equilibrium.

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Many chemical reactions go to completion because the products are much more energetically favourable than the reactants and the activation energy is low enough to allow for a rapid reaction at the ambient temperature, for example, the neutralisation of aqueous sodium hydroxide by hydrochloric acid. Other potential reactions do not occur either because, though energetically feasible, the activation energy barrier is too great for significant reaction at the ambient temperature (such as the combustion of sucrose at room temperature), or because as well as the activation energy being too high, the reactants are much more energetically stable than the products (as in the decomposition of water to hydrogen and oxygen). With some chemical systems however the energies of the reactants and products are of a similar order of magnitude so that the reaction is reversible, that is it can occur in either direction. An example is the reaction of ammonia and hydrogen chloride to form ammonium chloride. If ammonia gas and hydrogen chloride gas are mixed they react to form a white smoke of solid ammonium chloride.

Conversely if ammonium chloride is heated, then some of the solid 'disappears', because it has been converted into ammonia and hydrogen chloride gas. We indicate such a **reversible reaction** by means of a double arrow as shown below:



If such a system is established in a closed vessel (so that no gases can escape) and at a constant temperature, then a **chemical equilibrium** is established.

**Chemical equilibrium** is the state of dynamic equilibrium that occurs in a closed system when the forward and reverse reactions of a reversible reaction occur at the same rate. If we consider mixing together two reactants A and B in the **reversible reaction**:



then initially the forward reaction occurs rapidly, but as the concentrations of the reactants fall its rate decreases. The reverse reaction initially cannot occur at all, but as soon as C and D start to form, its rate increases. Eventually the rate of the two reactions becomes equal, the concentrations reach constant values and equilibrium is established. This is shown in Figure 701.

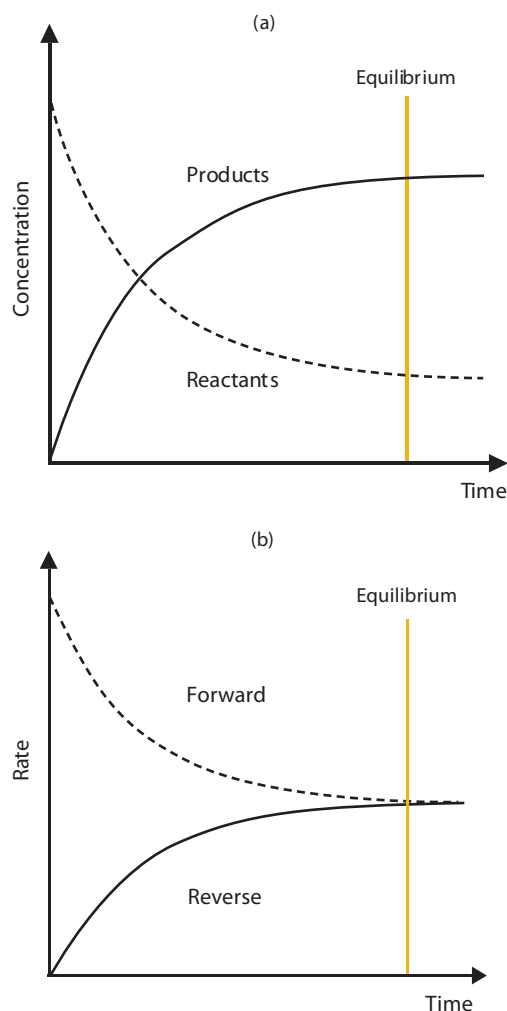


Figure 701 (a), (b) The change of concentration (a) and rate of reaction (b) with time in establishing a chemical equilibrium

In an equilibrium all of the species involved, both reactants and products, are present at a constant concentration. As a consequence, macroscopic properties of the system (that is those that can be observed or measured, such as its colour, density, pH) are constant, even though on a molecular scale there is continual interconversion of reactants and products. The concentrations of the species at equilibrium will reflect how readily they react on collision. If two species react on every collision, then the concentration required to produce a given rate of reaction will be much less than if they only have a 10% chance of reacting. In Figure 701 above, the reactants (A & B) react together far more easily than the products (C & D) because a smaller concentration is required to give the same rate of reaction. A similar equilibrium could obviously be established by mixing together C and D.

A specific example of such a system would be the introduction of one mole of liquid dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) into an evacuated, sealed one  $\text{dm}^3$  flask at  $\sim 80^\circ\text{C}$ .

The colourless dinitrogen tetroxide will initially vapourise and then start to decompose into brown nitrogen dioxide ( $\text{NO}_2$ ). The rate of this decomposition will fall as the concentration of dinitrogen tetroxide decreases. Initially there is no nitrogen dioxide present to dimerise, but as more is produced the rate of the reverse reaction to form dinitrogen tetroxide will increase. Eventually the two rates will become equal and chemical equilibrium is established as indicated by the fact that the brown colour of the gas does not change any further and the pressure in the flask remains constant. Under these conditions equilibrium would occur when about 60% of the dinitrogen tetroxide has been converted to nitrogen dioxide, so that the concentration of dinitrogen tetroxide will fall to  $0.4 \text{ mol dm}^{-3}$  and the concentration of nitrogen dioxide will increase to  $1.2 \text{ mol dm}^{-3}$ , because each dinitrogen tetroxide molecule decomposes to give two nitrogen dioxide molecules. This is shown in the equation below and in Figure 702.



Initial concentration	$1 \text{ mol dm}^{-3}$	$0 \text{ mol dm}^{-3}$
Equilibrium concentration	$0.4 \text{ mol dm}^{-3}$	$1.2 \text{ mol dm}^{-3}$

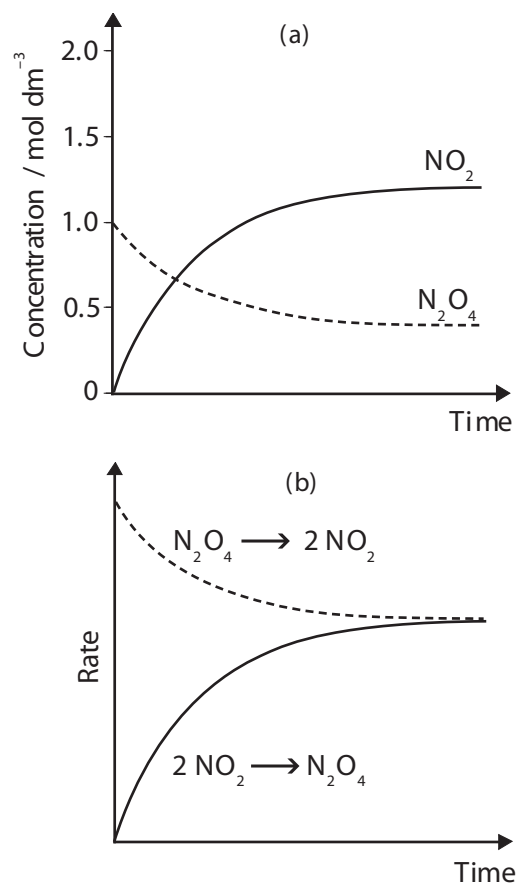


Figure 702 (a), (b) The equilibrium established by heating dinitrogen tetroxide

If 2 moles of nitrogen dioxide were cooled to 80 °C from a much higher temperature, at which there was no dinitrogen tetroxide present, then the brown colour would fade to a constant value, but eventually exactly the same position of equilibrium would be reached, as shown in Figure 703.

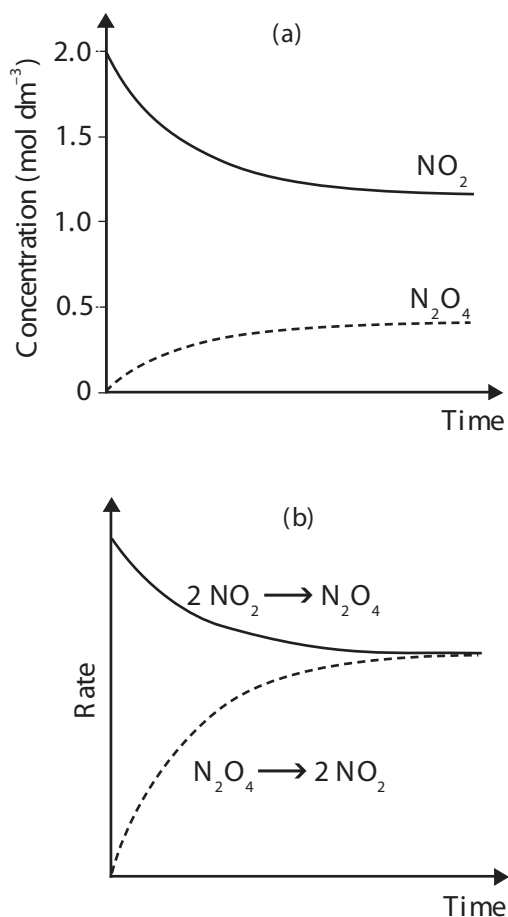


Figure 703 (a), (b) The equilibrium established by cooling nitrogen dioxide

### Exercise 7.1

- In a system at equilibrium, which of the following is not always true?
  - There are both reactants and products present.
  - The forward and reverse reactions occur at the same rate.
  - The concentrations of reactants and products are equal.
  - The concentrations of reactants and products remain constant.
- When solid phosphorus(V) chloride is heated it decomposes to solid phosphorus(III) chloride and chlorine gas. Conversely when phosphorus(III) chloride is shaken in an atmosphere of chlorine, it forms phosphorus(V) chloride.
  - Write a balanced equation for this reversible reaction, with phosphorus(V) chloride on the left hand side.
  - Consider warming some phosphorus(V) chloride in an empty, sealed flask:
    - What will happen to the phosphorus(V) chloride?
    - As time passes what will happen to the rate at which this occurs? Why?
    - Initially, what is the rate of reaction between phosphorus (III) chloride and chlorine? Why?
    - As time passes what will happen to the rate at which this occurs? Why?
    - Eventually what will happen to the rates of these two processes?
    - What name is given to this state?
    - At this point what species will be present in the flask? Will their concentrations all be equal?
  - Would there be a difference if the phosphorus(V) chloride was heated in an open beaker? If so explain why and predict what would in fact happen.

CORE

## 7.2 THE POSITION OF EQUILIBRIUM

## CORE

- 7.2.1 Deduce the equilibrium constant expression ( $K_c$ ) from the equation for a homogeneous reaction.
- 7.2.2 Deduce the extent of a reaction from the magnitude of the equilibrium constant.
- 7.2.3 Apply Le Chatelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant.
- 7.2.4 State and explain the effect of a catalyst on an equilibrium reaction.
- 7.2.5 Apply the concepts of kinetics and equilibrium to industrial processes.

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The rate at which a reaction occurs depends upon the concentration of the species involved. Let us make the assumption that both the forward and reverse reaction in the equilibrium



to be first order in each species (the final result can also be proved for a more general case, but the proof is much more complicated!) then the rate expressions for the forward and reverse reactions are:

$$\text{Forward rate} = k_f[A][B]$$

$$\text{Reverse rate} = k_r[C][D]$$

At equilibrium these rates are equal, so

$$k_f[A][B] = k_r[C][D] \text{ which rearranges to}$$

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

As  $k_f$  and  $k_r$  are constants, at a given temperature, their ratio must also be a constant. This is known as the equilibrium constant,  $K_c$ .

More generally, the **equilibrium constant** is given by the concentration of the products raised to the power of their stoichiometric coefficients (that is the numbers that appear before them in the balanced equation) divided by

the concentrations of the reactants also raised to these powers. For a general reaction:



The equilibrium constant is given by

$$K_c = \frac{[P]^p [Q]^q [R]^r \dots}{[A]^a [B]^b [C]^c \dots}$$

For example in the equilibrium between ammonia gas and oxygen gas to give nitrogen monoxide gas and water vapour:



The equilibrium constant is given by

$$K_c = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5} \text{ mol dm}^{-3}$$

The equilibrium constant does not have fixed units and they must be calculated in each case from the equation for  $K_c$ , using the fact that concentrations have units of  $\text{mol dm}^{-3}$ .

If the concentrations of the species involved were all  $1 \text{ mol dm}^{-3}$ , then  $K_c$  would have a value of one. If  $K_c$  is greater than one then the concentrations of products are greater than those of the reactants and the equilibrium is said to lie on the right hand side. If  $K_c$  is very large the reaction can be regarded as going to completion. If  $K_c$  is less than one the opposite is true and the equilibrium is said to lie on the left hand side. If  $K_c$  is very small, then the reaction may be considered not to occur.

The concentrations of certain substances remain constant, so these are omitted from the equilibrium constant expression. All solids have a fixed density and hence a constant concentration, so these are omitted. For example in the equilibrium:



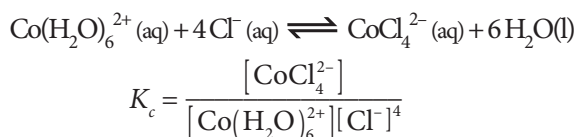
the equilibrium constant is simply given by

$$K_c = [\text{NH}_3][\text{HCl}] \text{ mol}^2 \text{ dm}^{-6}$$

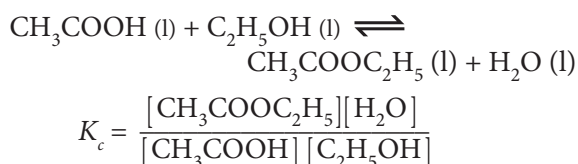
because the constant concentration of the solid ammonium chloride is omitted. The concentration of any pure liquid is also constant as it too has a fixed density. This is particularly important for the concentration of water

which is taken as constant and omitted for equilibria in dilute aqueous solutions.

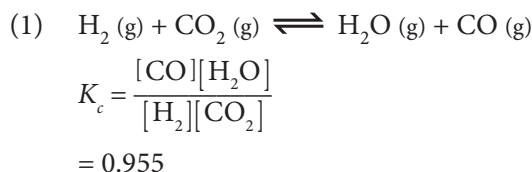
The equilibrium constant for the formation of the tetrachlorocobaltate(II) ion in dilute solution is therefore written as shown below:



If however the concentration of water can vary because the reaction is not in aqueous solution, for example in the equilibrium below, where the pure liquids would be mixed:

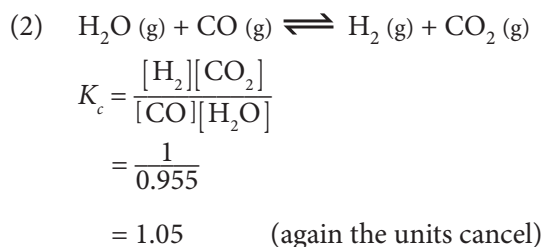


Water must also be included if it is in the gas phase, as for example in the reduction of carbon dioxide shown in equation (1) below, then the water must be included, for which the value for the equilibrium constant at 1000 K is given:

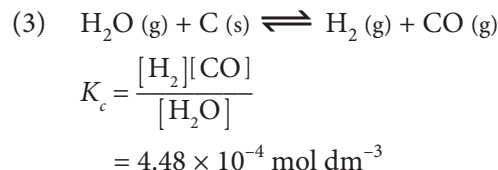


(Note - here  $K_c$  is unitless as the units cancel)

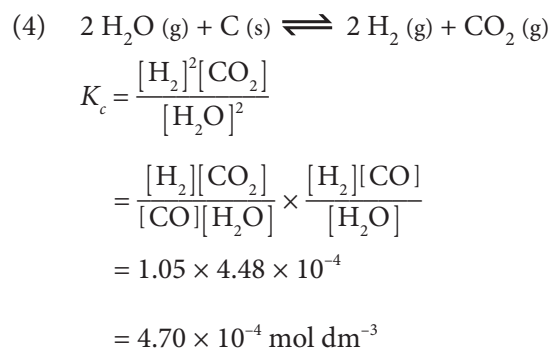
This equilibrium could easily be written the other way round, as shown in equation (2) below, and in this case the equilibrium constant is the reciprocal of the value given above:



Another interesting situation to consider is when the reactant in one equilibrium is the product of a previous equilibrium. For example the carbon monoxide in (2) could be the product of the reaction of carbon with steam shown in (3) below (the value of the equilibrium constant again being that at 1000 K):



These two equilibria can then be combined, as shown in (4) and in this case the equilibrium constant is the product of those for the two separate equilibria:



## THE EFFECT OF CONDITIONS ON THE POSITION OF EQUILIBRIUM

If the conditions (such as temperature, pressure, or the concentrations of the species involved) under which the equilibrium is established are changed, then the rates of the forward and reverse reactions will no longer be equal. As a result the equilibrium is disturbed and the concentrations of the species will change until the rates once again become equal and equilibrium is once more established.

**Le Chatelier's principle** is a way of predicting the direction (forward or reverse) in which the position of equilibrium will change if the conditions are altered. It states

*“If a change is made to the conditions of a chemical equilibrium, then the position of equilibrium will readjust so as to minimise the change made.”*

This means that increasing a concentration of a species will result in a change that will cause that concentration to decrease again; increasing pressure will result in a change that will cause the pressure to decrease again; increasing the temperature will result in a change that will cause the temperature to decrease again. The effects of changes in the conditions of equilibrium are summarised in Figure 704.

Note that whilst changes in concentration and pressure affect the position of equilibrium and the amounts of the

Change	Effect on Equilibrium	Does $K_c$ change?
Increase concentration	Shifts to the opposite side	No
Decrease concentration	Shifts to that side	No
Increase pressure	Shifts to side with least moles of gas	No
Decrease pressure	Shifts to side with most moles of gas	No
Increase temperature	Shifts in endothermic direction	Yes
Decrease temperature	Shifts in exothermic direction	Yes
Add catalyst	No effect	No

Figure 704 The effect of changes in conditions on the position of an equilibrium

various species present, they have no effect on the value of the equilibrium constant,  $K_c$ , because the values of the forward and reverse rate constants  $k_f$  and  $k_r$ , respectively do not change. A change in temperature does however affect the rate constants, so that the value of  $K_c$  changes as well as the position of equilibrium.

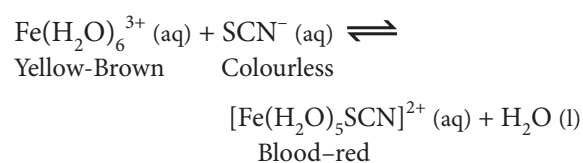
If an unreactive gas is added to a fixed volume of the equilibrium, so all concentrations remain constant, then there is no effect. If however the gas is added at a constant pressure, so that the total volume has to increase, then the concentrations of all species will decrease, so the effect is similar to that of reducing the total pressure.

The presence of a catalyst reduces the activation energy of both the forward and reverse reactions by the same amount. This means that both the forward and reverse reactions are speeded up by the same factor, so even though the equilibrium is established more rapidly, neither the position of equilibrium nor the value of the equilibrium constant are affected.

## Concentration

If the concentration of a species is increased, then the equilibrium moves towards the other side causing the concentration to fall to a value between the original concentration and the increased value. Conversely if the concentration of a species is reduced the equilibrium shifts towards the side of the equilibrium on which it occurs causing its concentration to increase to a value between the original concentration and the reduced value.

Consider the equilibrium:



If aqueous thiocyanate ions are added to an aqueous solution of an iron(III) salt, then a blood-red colouration is observed owing to the formation of the complex ion shown. If the concentration of either the thiocyanate ion or the iron(III) ion is increased, then the intensity of the colouration increases. This is in keeping with Le Chatelier's principle because the shift of the equilibrium to the right causes the concentration of the added reactant to fall again. It also shows that the reaction has not gone to completion because addition of either reactant causes an increase in the amount of product. If the concentration of iron(III) ions is decreased by adding fluoride ions (which form the very stable  $\text{FeF}_6^{3-}$  complex ion) then the intensity of the colouration decreases. This is in keeping with Le Chatelier's principle because the shift of the equilibrium to the left produces more aqueous iron(III) ions to counteract the reduction caused by the fluoride ions. It also shows that the reaction is reversible. Note that even though the position of equilibrium is altered, the change in concentrations is such that the value of  $K_c$  remains unchanged.

## Pressure

If the total pressure of a system (P) is increased then the equilibrium shifts to the side with least moles of gas, so causing the pressure to fall to a value between the original pressure and the increased value. Conversely if the total pressure of the system is reduced the equilibrium shifts towards the side with the most moles of gas, causing the pressure to increase to a value between the original pressure and the reduced value. Consider the examples below:

$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$   
 3 moles of gas is converted to 2 moles of gas  
 Increased P, equilibrium  $\rightarrow$ ;  
 Decreased P, equilibrium  $\leftarrow$

$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$   
 1 mole of gas is converted to 2 moles of gas  
 (note: carbon is a solid)  
 Increased P, equilibrium  $\leftarrow$ ;  
 Decreased P, equilibrium  $\rightarrow$

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$   
 2 moles of gas is converted to 2 moles of gas  
 Changing P has no effect

Note that even though the position of equilibrium is altered, the changes in the concentrations that result from the changes in pressure are such that the value of  $K_c$  remains unchanged.

## Temperature

If the temperature of a system is increased then the equilibrium shifts in the direction of the **endothermic change**, so absorbing heat and causing the temperature to fall to a value between the original temperature and the increased value. Conversely if the temperature of the system is reduced the equilibrium shifts in the direction of the **exothermic change**, so releasing heat and causing the temperature to increase to a value between the original temperature and the reduced value. Consider the examples below:

$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$   
 $\Delta H = +180 \text{ kJ mol}^{-1}$   
 (i.e. forward reaction endothermic)  
 Increased  $T$ ,  $K_c$  increases, equilibrium  $\rightarrow$ ;  
 Decreased  $T$ ,  $K_c$  decreases, equilibrium  $\leftarrow$

$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$   
 $\Delta H = -197 \text{ kJ mol}^{-1}$   
 (i.e. forward reaction exothermic)  
 Increased  $T$ ,  $K_c$  decreases, equilibrium  $\leftarrow$ ;  
 Decreased  $T$ ,  $K_c$  increases, equilibrium  $\rightarrow$

Note that changes in temperature affect the rate constants of the forward and reverse reactions to different extents, so the actual value of  $K_c$  changes.

## EXPLANATIONS

Le Chatelier's principle is just a memory aid that helps us to predict the effect that a change in conditions will have on the position of an equilibrium. It is **not** an explanation of **why** these changes occur. The explanation come from a consideration of the effect of the change in conditions on the rates of the forward and reverse reactions.

Consider the effects of the changes in conditions on the equilibrium between solid phosphorus pentachloride, liquid phosphorus trichloride and gaseous chlorine:



If the concentration of chlorine is increased, then the rate of the reverse reaction will increase, but the forward reaction will be unaffected, so that the reaction rates are no longer equal. In order for equilibrium to be restored, the amount of the pentachloride must increase and the amount of the trichloride decrease so that the position of the equilibrium will shift to the left, hence the amount of chlorine decreases to below its new higher level, but still above the original level (see Figure 705). This is in agreement with the predictions of Le Chatelier's principle that the position of equilibrium will shift to the opposite side to the species whose concentration has been increased. Obviously a decrease in the concentration of chlorine has the opposite effect, though neither affects the value of  $K_c$ .

If the total pressure is increased then the rate of the reverse reaction will again increase, because this is the only one that involves a gas and an increase in pressure only increases the concentration of gases. The more moles of gas involved on the side of the equilibrium, the more a change in pressure will affect the rate. The result of this increase in the rate of the reverse reaction is the same as those explained above and the position of equilibrium will again shift to the left. This results in a reduction in the amount of chlorine and hence the total pressure falls below the new higher value (see Figure 706). A decrease in total pressure will have the opposite effect, but once again the value of  $K_c$  is unchanged.

If the temperature is increased, then the rates of both the forward and reverse reactions will increase, but they will not do so by the same amount. The higher the activation energy, the greater the effect of temperature on reaction rate, so that an increase in temperature will speed up the reaction in the endothermic direction (which must have the greater activation energy) more than the exothermic reaction. In this example the forward reaction is endothermic ( $\Delta H$  positive), so the reverse reaction is exothermic. The effect of an increase in temperature is therefore to increase the rate constant of the forward

reaction more than that of the reverse reaction. Therefore, the value of  $K_c$  increases and the reaction shifts to the right, producing more chlorine and phosphorus trichloride until the reaction rates again become equal (see Figure 707). This endothermic change absorbs heat energy and causes the temperature of the system to fall to below its new higher value. A decrease in temperature will have the opposite effect and the value of  $K_c$  will decrease.

Figures 705, 706 and 707 show the effect of changes in conditions on the equilibrium established by heating phosphorus pentachloride.

## INDUSTRIAL PROCESSES

Many industrial processes involve equilibria. The aim of the process is to produce the desired product as efficiently as possible, that is rapidly, but with the minimum amount of waste and the minimum input of energy. This requires a study of both kinetics (how fast the product is made from the reactants) and equilibrium (how much of the desired product is present in the mixture produced) considerations. Two processes to which these considerations have been applied are the Haber Process, for the production of ammonia, and the Contact Process, for the production of sulfuric acid. These are considered separately in Figure 707.

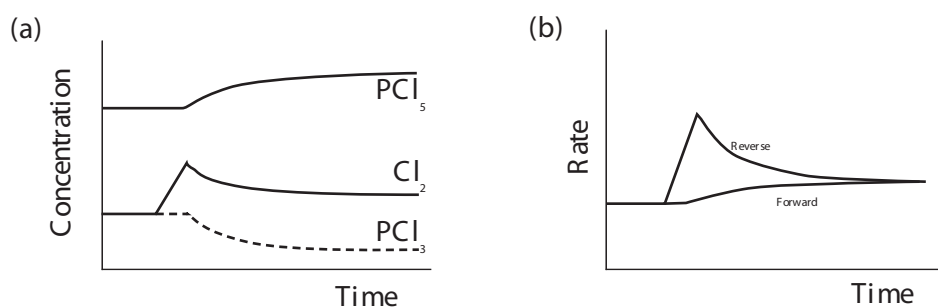


Figure 705 Increased concentration of chlorine

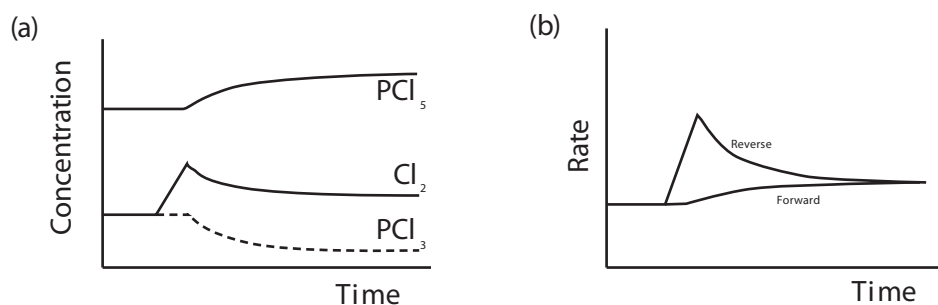


Figure 706 Increased total pressure

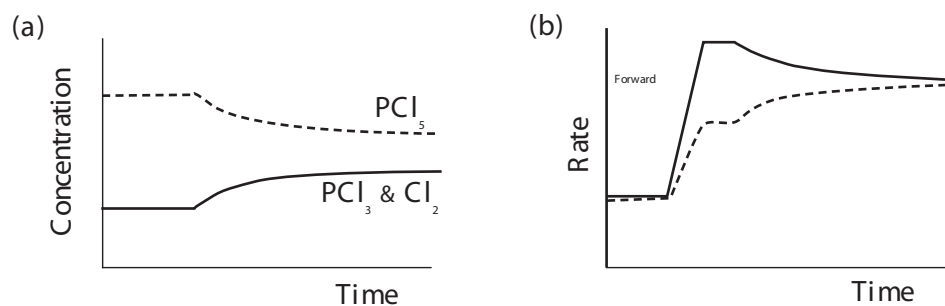
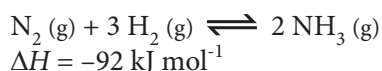


Figure 707 Increased temperature

(N.B. the 'flat' sections on the rate graph have been exaggerated to distinguish between the effects of temperatures and concentration changes)

## Haber Process

The Haber process involves the direct combination of nitrogen and hydrogen to produce ammonia. A mixture of nitrogen and hydrogen in a 1:3 ratio by volume is compressed and passed over a heated iron catalyst where the following equilibrium is established.



The choice of conditions for this equilibrium is critical. It can be seen that in the reaction 4 moles of gas are converted to 2 moles of gas, hence a high pressure will favour the formation of the product, as Figure 708 confirms. The provision of a high pressure is however expensive, both in terms of the capital cost of providing a plant that will resist high pressures and in terms of the operating costs of compressing gases to high pressures. The final choice will therefore be a compromise pressure that takes into account these factors.

It can be seen from the equation above that the forward reaction is exothermic ( $\Delta H$  is negative), hence a low temperature would favour the products, as can be seen from Figure 708. Unfortunately low temperatures result in low rates of reaction so that even though there may be a high proportion of ammonia in the product it may take a long time for the conversion to occur. A compromise temperature is therefore chosen so as to produce the maximum mass of ammonia per hour. The use of a finely divided catalyst containing iron also increases the reaction rate.

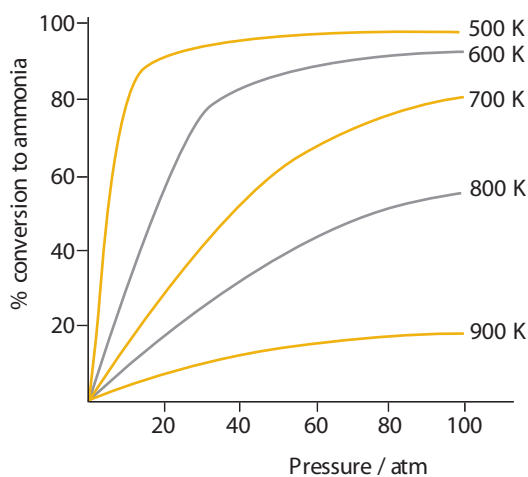
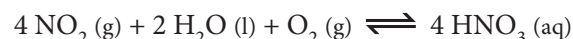
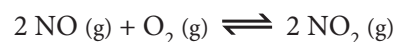


Figure 708 The effect of conditions on the proportion of ammonia at equilibrium

Typical conditions chosen for the Haber process are pressures in the range 200 – 1000 atm (20 – 100 MPa) and temperatures  $\approx 700$  K. The reaction is however not left for sufficient time to reach equilibrium (remember the

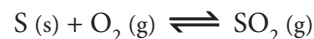
reaction rate will decrease as equilibrium is approached – see Figure 701) and typically in the converter only about 20% of the nitrogen and hydrogen is converted to ammonia. It would be very uneconomical to waste the unchanged reactants, so the mixture of gases is cooled causing the ammonia to condense (it can hydrogen bond, unlike the reactants) so that it can be separated and the gaseous nitrogen and hydrogen recycled.

Nitrogen is an element vital for plant growth, so the major use of ammonia is the manufacture of fertilizers, such as ammonium salts and urea. It is also used in the manufacture of nitrogen containing polymers such as nylon. Ammonia can also be oxidised to produce nitric acid, involving the initial oxidation of ammonia over a platinum catalyst (see the equations below), which is used in the production of explosives such as TNT, dynamite etc. and in the dye industry.

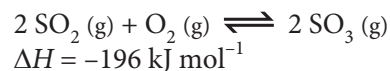


## Contact Process

The Contact process is the production of sulfuric acid by the oxidation of sulfur. Firstly pure sulfur is burnt in air to form sulfur dioxide:



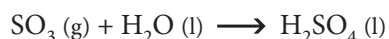
Sulfur dioxide is mixed with air and passed over a vanadium(V) oxide catalyst to produce sulfur trioxide:



As with the Haber Process a high pressure would favour the formation of the product (3 moles of gas going to 2), but in this case excellent conversion is achieved without the expense of a high pressure process. Hence the reactants are only compressed to the pressure needed (about 2 atm) to achieve the desired flow rate in the reactor. Similarly using pure oxygen rather than air would drive the equilibrium to the right, but again it would be an unnecessary expense. Another similarity is that the forward reaction is exothermic, so a low temperature favours the products. As with the Haber Process the temperature cannot be too low otherwise the process becomes uneconomically slow. The result is the choice of a compromise temperature (700 – 800 K) and the use of a catalyst (finely divided  $\text{V}_2\text{O}_5$ ) to enhance the reaction rate. Also the oxidation to sulfur trioxide is usually done by a number of converters at

successively lower temperatures, so as to make use of high temperature to give a fast initial rate of reaction as well as a low temperature to give a high final equilibrium yield. The result is well over 90% conversion to the trioxide. After absorption of the sulfur trioxide, the gases are often passed through one more converter to ensure that the waste gases contain so little sulfur dioxide that they can be released directly into the air.

The sulfur trioxide must now be reacted with water to produce sulfuric acid:



Sulfuric acid has numerous uses in the chemical industry – indeed the tonnage of it used annually gives a good indication of the extent of a country's chemical industry. These uses include manufacture of fertilizers (especially converting insoluble phosphate rock to soluble 'superphosphate'), polymers, detergents, paints and pigments. It is also widely used in the petrochemicals industry and in the industrial processing of metals. One of its minor, though possibly most familiar uses, is as the electrolyte in automobile batteries.

### Exercise 7.2

- The equilibrium constant for a reaction that occurs totally in the gas phase is given below. What is the chemical equation for this equilibrium?
 
$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$$
  - $\text{CO}_2(\text{g}) + \text{CF}_4(\text{g}) \rightleftharpoons \text{COF}_2(\text{g})$
  - $\text{CO}_2(\text{g}) + \text{CF}_4(\text{g}) \rightleftharpoons 2 \text{COF}_2(\text{g})$
  - $2 \text{COF}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CF}_4(\text{g})$
  - $\text{COF}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CF}_4(\text{g})$
- Which one of the following will increase the rate at which a state of equilibrium is attained without affecting the position of equilibrium?
  - Increasing the temperature.
  - Increasing the pressure.
  - Decreasing the concentration of the products.
  - Adding a catalyst.
- In the manufacture of methanol, hydrogen is reacted with carbon monoxide over a catalyst of zinc and chromium oxides and the following equilibrium is established:
 
$$2 \text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$$

$$\Delta H = -128.4 \text{ kJ mol}^{-1}$$

Which one of the following changes would increase the percentage of carbon monoxide converted to methanol at equilibrium?

  - Decreasing the total pressure.
  - Increasing the temperature.
  - Increasing the proportion of hydrogen in the mixture of gases.
  - Increasing the surface area of the catalyst.
- When heated in a sealed vessel, ammonium chloride is in equilibrium with ammonia and hydrogen chloride according to the equilibrium:
 
$$\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$$

Increasing the temperature increases the proportion of the ammonium chloride that is dissociated. The best explanation of this observation is that:

  - this increases the rate of both reactions, but the forward reaction is affected more than the reverse reaction.
  - this increases the rate of both reactions, but the reverse reaction is affected more than the forward reaction.
  - this increases the rate of the forward reaction, but decreases the rate of the reverse reaction.
  - this decreases the rate of both reactions, but the reverse reaction is affected more than the forward reaction.
- When methane and steam are passed over a heated catalyst the equilibrium below is established.
 
$$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3 \text{H}_2(\text{g})$$

Which one of the following will result in a change in the value of the equilibrium constant ( $K_c$ )?

  - Increasing the pressure.
  - Adding more methane ( $\text{CH}_4$ ).
  - Decreasing the concentration of steam.
  - Increasing the temperature.

6. When  $0.1 \text{ mol dm}^{-3}$  aqueous solutions of silver nitrate and iron(II) nitrate are mixed, the following equilibrium is established:

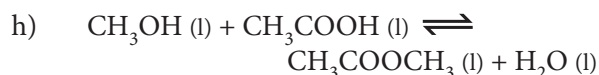
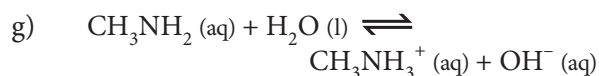
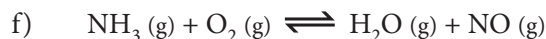
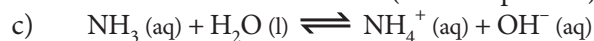
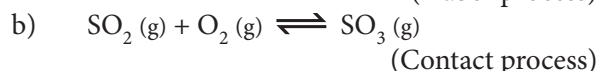
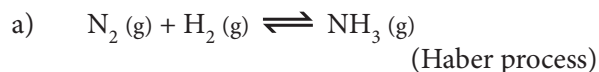


Which of the following changes would produce more silver?

- A Adding some iron(III) nitrate solution.  
 B Adding more iron(II) nitrate solution.  
 C Removing some of the  $\text{Ag}^+$  ions by forming insoluble silver chloride.  
 D Increasing the total pressure.
7. In the conversion of nitrogen to ammonia using the Haber process, the main reason why the temperature is limited to about  $450 \text{ }^\circ\text{C}$  is because

- A a higher temperature would cause the catalyst to break down.  
 B a higher temperature would cause the reaction to occur too slowly.  
 C a higher temperature would decrease the amount of ammonia present at equilibrium.  
 D a higher temperature would cost too much money to maintain.

8. For each of the following equilibrium reactions, balance the equation with whole number coefficients and deduce its  $K_c$  expression:



9. The central reaction in the Haber process is the equilibrium between nitrogen, hydrogen and ammonia.

- a) Write a balanced equation for this equilibrium.  
 b) The enthalpy change in this reaction is  $-92.6 \text{ kJ mol}^{-1}$  and the activation energy is  $+335 \text{ kJ mol}^{-1}$ . Draw an energy level diagram for this equilibrium.  
 c) The reaction usually takes place in the presence of an iron catalyst. On the diagram from b), mark the reaction pathway for the catalysed reaction with a dotted line.  
 d) Would you expect the iron to be present as solid lumps or in a finely divided state? Explain why.  
 e) The reaction is usually carried out at a pressure well above atmospheric pressure. How would you expect this to affect the rate of reaction? Explain why it has this effect.

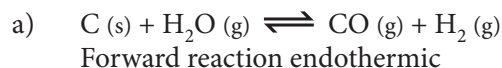
10. Nitrogen monoxide and oxygen react together in a reversible reaction to form nitrogen dioxide.

- a) Describe, in terms of the rates of the reactions and the concentrations of the species present, the way in which equilibrium is established if nitrogen monoxide and oxygen are suddenly mixed in an empty flask.  
 b) Write a balanced equation for this equilibrium.  
 c) Nitrogen dioxide is brown, whereas nitrogen monoxide is colourless. If the oxygen is replaced with an equal volume of air, the mixture of gases becomes lighter coloured. Explain why this occurs.

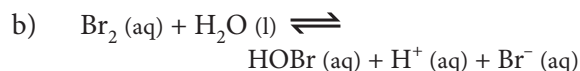
11. For each of the following equilibria, state:

I whether change (i) would shift the position of equilibrium to the right or the left.  
 and

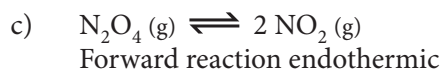
II how you could change the second factor (ii) so as to shift the position of equilibrium in the opposite direction.



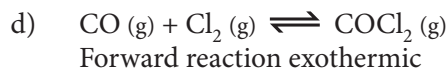
- (i) increasing the total pressure.  
 (ii) changing the temperature.



- (i) adding potassium bromide.  
 (ii) changing the pH.



- (i) decreasing the temperature.  
(ii) changing the total pressure.



- (i) adding more chlorine.  
(ii) changing the temperature.



- (i) reducing the pressure.  
(ii) changing the concentration of ammonia.

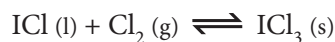
12. A gaseous mixture of hydrogen, iodine and hydrogen iodide are in equilibrium according to the equation:



State how the position of equilibrium will be affected by the following changes and explain your reasoning:

- a) Decreasing the temperature.  
b) Adding more hydrogen at constant pressure.  
c) Increasing the total pressure.

13. A flask contains iodine monochloride, a brown liquid, iodine trichloride, a yellow solid, and chlorine gas in equilibrium according to the equation:



- a) If the volume of the flask was reduced so as to increase the total pressure, explain what you would expect to happen to the amounts of brown liquid and yellow solid?  
b) When the flask is cooled in iced water the amount of yellow solid increases and there is less brown liquid. Explain what this shows about the equilibrium?

14. Sulfuric acid is manufactured by the reaction between sulfur trioxide and water. The sulfur trioxide is formed by the reaction of sulfur dioxide and oxygen from air in the presence of a catalyst. This is known as the Contact process and establishes an equilibrium in which the forward reaction is exothermic.

- a) Write a balanced equation for the equilibrium.

- b) What effect does the catalyst have upon:  
i) the rate of the forward reaction?  
ii) the rate of the reverse reaction?  
iii) the proportion of sulfur dioxide converted to sulfur trioxide?  
c) If a high pressure was used, what effect would this have on the relative proportions of sulfur dioxide and sulfur trioxide? Explain.  
d) Much greater reaction rates could be achieved if the temperature was increased. Explain why this is not done.

## HIGHER LEVEL

### 17.1 LIQUID-VAPOUR EQUILIBRIUM (AHL)

17.1.1 Describe the equilibrium established between a liquid and its own vapour and how it is affected by temperature changes.

17.1.2 Sketch graphs showing the relationship between vapour pressure and temperature and explain them in terms of the kinetic theory.

17.1.3 State and explain the relationship between enthalpy of vapourization, boiling point and intermolecular forces.

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Consider an evacuated container with a layer of a volatile liquid in the bottom of it. Molecules of the liquid will escape from the surface and enter the vapour phase. These molecules in the vapour phase will collide with the walls of the container and exert a pressure. Some of the molecules will also strike the surface of the liquid and condense back into the liquid phase. Initially this rate of return will be low, but as more and more molecules escape into the vapour phase and the pressure increases, the rate of return also increases until it becomes equal to the rate at which the particles vapourise from the surface so that

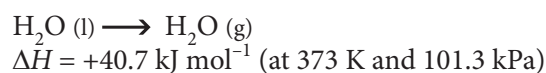
$$\text{Rate of vapourisation} = \text{Rate of condensation}$$

At this point the system is in a state of dynamic equilibrium, similar to a chemical equilibrium, and the pressure exerted by the particles in the vapour phase is known as the **vapour pressure** of the liquid. Altering the surface

area of the liquid affects both of the rates equally, so that it has no overall effect on the vapour pressure, though it will affect the time taken to reach equilibrium - the greater the surface area, the more rapidly equilibrium is achieved.

Molecules on the surface need a certain minimum amount of kinetic energy before they can escape from the attractive forces of the other surface molecules. This will depend on the strength of the intermolecular forces and is similar to the concept of activation energy for a chemical reaction. Vapourisation is an endothermic process, as it requires the overcoming of the attractive forces between the particles. The amount of energy required for this phase change is known as the enthalpy of vapourisation.

More precisely the **enthalpy of vapourisation** is the amount of energy required to convert one mole of the substance from the liquid to the gaseous state. Using water as an example, it is the enthalpy change associated with the transition:



This energy is mainly required to overcome intermolecular forces, though some is required to do work against the atmosphere. When a substance boils, its temperature does not increase (there is no increase in kinetic energy), so that the energy absorbed is involved in increasing potential energy by overcoming attractive forces between the particles.

The stronger the forces between the particles, the greater the enthalpy of vapourisation, the lower the vapour pressure at a given temperature, and the higher the boiling point. This is illustrated by the data in Figure 710.

Compound	Enthalpy of vapourisation / $\text{kJ mol}^{-1}$	Boiling point / K	Intermolecular forces
Methane	9.0	109	van der Waals' only
Methoxymethane	27.2	248	van der Waals' and dipole-dipole
Ethanol	38.6	352	van der Waals', dipole-dipole, and hydrogen bonds

Figure 710 Enthalpy of vapourisation and boiling point data of some compounds

At a higher temperature, more molecules will have the required kinetic energy to escape into the vapour phase and the rate of vapourisation will increase (see Figure 711). This means that more molecules are required in the gas phase for the rate of condensation to equal the rate of vapourisation, hence an increase in temperature results in an increase in vapour pressure, as shown in Figure 711. A liquid will boil when its vapour pressure is equal to the pressure on the surface of the liquid, because this allows bubbles of vapour to form in the body of the liquid. The normal **boiling point** is the temperature at which the vapour pressure is equal to standard atmospheric pressure (101.3 kPa), as shown in Figure 711. A liquid will, however, boil at a lower temperature if the external pressure is reduced, as would be the case on top of a mountain. Similarly if the external pressure is increased, as in a pressure cooker, the boiling point of the liquid increases.

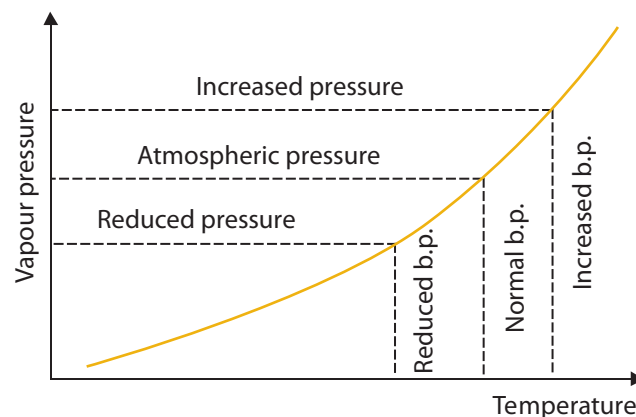


Figure 711 The relationship between temperature and vapour pressure showing the boiling point

## 17.2 THE EQUILIBRIUM LAW (AHL)

### 17.2.1 Solve homogeneous equilibrium problems using the expression for $K_c$ .

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A **homogeneous equilibrium** is one in which all the reactants and products are in the same phase. If there are two or more phases then it is a **heterogeneous equilibrium**. The concentrations, when substituted into the equilibrium constant formula, will only equal the equilibrium constant if the system is in fact at equilibrium. For other situations, when equilibrium is not present, the value produced by treating the concentrations in the same way as the equilibrium constant (sometimes referred to as the reaction quotient,  $Q_c$ ) will indicate which way the reaction needs to shift in order to attain equilibrium. If  $Q_c > K_c$ , then the value of  $Q_c$  must fall, hence some products must be converted to reactants and the system must shift to the left (in the reverse direction) until  $Q_c = K_c$  and equilibrium is established. Conversely if  $Q_c < K_c$ , then the system must shift to the right (in the forward direction) and some reactants must be converted to products until  $Q_c = K_c$  and equilibrium is established. Consider the reaction:



$$K_c = 0.955 \text{ at } 1000 \text{ K}$$

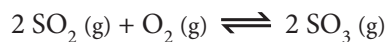
If equal amounts of the gases are mixed at 1000 K then  $Q_c = 1$ , which is greater than  $K_c$  at this temperature, so the system must shift to the left (in the reverse direction) to achieve equilibrium. In other words, some of the water and carbon monoxide will react to form carbon dioxide and hydrogen, altering the concentrations so that  $Q_c = K_c$ .

As with any mathematical expression, if all of the terms except one in the equilibrium expression are known, the unknown term may be calculated by substitution. This is best illustrated by means of examples:

#### Example

When a mixture initially containing  $0.0200 \text{ mol dm}^{-3}$  sulfur dioxide and an equal concentration of oxygen is allowed to reach equilibrium in a container of fixed volume at 1000 K, it is found that 80.0% of the sulfur dioxide is converted to sulfur trioxide. Calculate the value of the equilibrium constant at that temperature.

#### Solution



Assuming, for simplicity, a volume of  $1 \text{ dm}^3$ , then as 80% of the sulfur dioxide turns into the trioxide:

$$\begin{aligned} \text{Equilibrium } [\text{SO}_3] &= 0.0200 \times 0.800 \\ &= 0.0160 \text{ mol dm}^{-3} \end{aligned}$$

Each sulfur trioxide molecule is formed from one sulfur dioxide molecule, so:

$$\begin{aligned} \text{Equilibrium } [\text{SO}_2] &= 0.0200 - 0.0160 \\ &= 0.0040 \text{ mol dm}^{-3} \end{aligned}$$

Each sulfur trioxide molecule requires only half an oxygen molecule, so:

$$\begin{aligned} \text{Equilibrium } [\text{O}_2] &= 0.0200 - (\frac{1}{2} \times 0.0160) \\ &= 0.0120 \text{ mol dm}^{-3} \end{aligned}$$

Substituting into the equilibrium constant expression, the value of the equilibrium constant may be calculated:

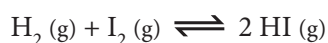
$$\begin{aligned} K_c &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \\ &= \frac{0.0160^2}{0.0040^2 \times 0.0120} \\ &= 1333 \\ &= 1330 \text{ mol}^{-1} \text{ dm}^3 \text{ (3 s.f.)} \end{aligned}$$

Similarly if the equilibrium constant is known, then given appropriate information the equilibrium or starting concentration of one of the reactants may be found, the best technique usually being to substitute 'x' for the unknown quantity. In many cases though the resulting equation may contain powers of 'x' and hence require special techniques for their solution. This is not however the case with the example given below:

## Example 2

In the gas phase at 730 K, the equilibrium constant for the reaction of hydrogen and iodine to form hydrogen iodide has a value of 490. If the initial concentration of iodine is  $0.0200 \text{ mol dm}^{-3}$ , what concentration of hydrogen is required for 90.0% of the iodine to be converted to hydrogen iodide?

## Solution



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Initial  $[\text{I}_2] = 0.0200$ , so at equilibrium, if 90.0% converted,  
 $[\text{I}_2]_{\text{eq}} = (0.0200 - 0.0180) = 0.0020$

Concentration of  $\text{I}_2$  converted =  $0.0200 - 0.00200$

$$= 0.0180 \text{ mol dm}^{-3}$$

$\therefore$  Concentration of HI formed =  $2 \times 0.0180$  (1 mole of  $\text{I}_2$  forms 2 moles of HI)

$$= 0.0360 \text{ mol dm}^{-3}$$

If the initial concentration of  $\text{H}_2 = x$ ,

then equilibrium concentration of  $\text{H}_2\text{I}_2$

$$= [\text{H}_2\text{I}_2]_{\text{eq}} = x - 0.0180$$

Substituting:

$$490 = \frac{0.0360^2}{(x - 0.0180) \times 0.00200}$$

$$x - 0.0180 = \frac{0.0360^2}{490 \times 0.00200}$$

$$= 0.00132$$

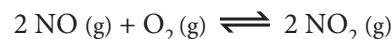
$$x = 0.00132 + 0.0180$$

$$= 0.01932$$

$$= 0.0193 \text{ mol dm}^{-3} \text{ (3 s.f.)}$$

## Exercise 17.2

1. At a particular temperature, a mixture of nitrogen monoxide and oxygen is allowed to reach equilibrium according to the equation:



The equilibrium concentrations of the gases are  $0.03 \text{ mol dm}^{-3}$  nitrogen monoxide;  $0.04 \text{ mol dm}^{-3}$  oxygen and  $0.02 \text{ mol dm}^{-3}$  nitrogen dioxide. What is the value of the equilibrium constant,  $K_c$ ?

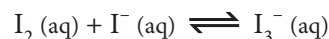
A  $\frac{0.3 \times 0.04}{0.02} \text{ mol dm}^{-3}$

B  $\frac{0.02}{0.03 \times 0.04} \text{ mol}^{-1} \text{ dm}^3$

C  $\frac{0.02}{0.03 \times 0.04^2} \text{ mol}^{-2} \text{ dm}^6$

D  $\frac{0.02^2}{0.03^2 \times 0.04} \text{ mol}^{-1} \text{ dm}^3$

2. When 0.01 moles of iodine are added to  $1 \text{ dm}^3$  of  $0.2 \text{ mol dm}^{-3}$  aqueous potassium iodide, 99% is converted to the triiodide ion according to the equilibrium



What is the approximate value of the equilibrium constant?

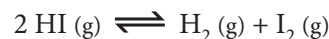
A  $500 \text{ mol}^{-1} \text{ dm}^3$

B  $100 \text{ mol}^{-1} \text{ dm}^3$

C  $2 \text{ mol}^{-1} \text{ dm}^3$

D  $0.002 \text{ mol}^{-1} \text{ dm}^3$

3. The equilibrium constant for the dissociation of hydrogen iodide into its elements, according to the equation below, at 900 K is 0.04.



If the equilibrium concentration of hydrogen iodide is  $0.2 \text{ mol dm}^{-3}$ , what is the approximate equilibrium concentration of iodine?

A 0.3

B 0.04

C 0.008

D 0.0016

4. When ammonium hydrosulfide is heated it dissociates according to the equilibrium below. The value of  $K_c$  for this equilibrium at a particular temperature is  $0.00001 \text{ mol}^2 \text{ dm}^{-6}$ .



- Explain the units of the equilibrium constant.
  - Calculate the concentration of ammonia at equilibrium.
  - If some ammonia gas was injected at constant pressure and temperature, how would this affect
    - the mass of solid present?
    - the concentration of hydrogen sulfide?
    - the value of  $K_c$ ?
5. When nitrogen and hydrogen react together in the presence of a catalyst, they produce ammonia. The following table gives the percent of ammonia in the mixture when a 3:1  $\text{H}_2:\text{N}_2$  mixture reaches equilibrium under various conditions:

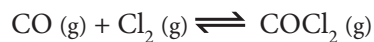
Pressure / MPa	10	20
Temperature / °C		
400	25%	36%
500	10%	17%

- What do these data show about the equilibrium?
- At 10 MPa and 400°C, the equilibrium concentrations of the species present are:
 
$$[\text{N}_2] = 0.335 \text{ mol dm}^{-3},$$

$$[\text{H}_2] = 1.005 \text{ mol dm}^{-3},$$

$$[\text{NH}_3] = 0.450 \text{ mol dm}^{-3}.$$
 Calculate a value for the equilibrium constant and give appropriate units.

6. For the gaseous equilibrium:



- Write the expression for the equilibrium constant  $K_c$ .
- The concentrations of the various species at a particular temperature are given below. Calculate the value of the equilibrium constant  $K_c$ , giving appropriate units.
 
$$[\text{CO}] = 0.800 \text{ mol dm}^{-3};$$

$$[\text{Cl}_2] = 0.600 \text{ mol dm}^{-3};$$

$$[\text{COCl}_2] = 0.200 \text{ mol dm}^{-3}$$
- If the pressure of the system is suddenly increased so that the volume halves, calculate the new concentrations.
- If these are substituted into the equilibrium constant expression, what is the numerical result.
- Is the system still at equilibrium? If not in which direction will the reaction proceed? How did you deduce this?
- Is this consistent with Le Chatelier's principle? Explain.

## EXTENSIONS

### THE VAPOUR PRESSURE OF MIXTURES

If the system contains two components that do not mix (for example, water and trichloromethane), they will each exert their own vapour pressure, provided it is shaken so both come into contact with the vapour phase. In other words the total vapour pressure is the sum of the individual vapour pressures. The situation is just the same as if one side of the container contained one component and the other side the other component, because particles of a particular substance can only leave from, and return to their own surface.

If the system contains two substances that do mix, then both of them will have vapour pressures in the mixture that are lower than in the pure liquids. This is because there will be less molecules of each component near the surface, reducing the rate of escape, but all of the surface is available for particles in the gas phase to return to, hence the rate of return is unaffected by being a mixture. If both of the liquids are volatile, then the total vapour pressure is the sum of these reduced vapour pressures and this provides the basis for fractional distillation (see below). If however one of the components is non-volatile, as is usually the case for a solid dissolved in a liquid, then the total vapour pressure of the system will be reduced, as shown in Figure 712, and this is the basis for the elevation of boiling point and depression of freezing point.

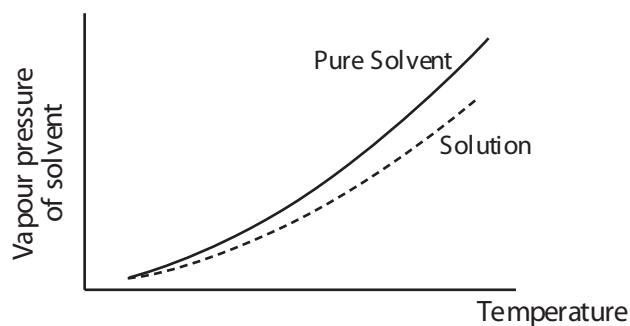


Figure 712 Illustrating the effect of a dissolved solid on the vapour pressure of a solvent

### DISTILLATION AND FRACTIONAL DISTILLATION

A volatile liquid can be separated from a non-volatile solute by **simple distillation**. The apparatus for this is shown in Figure 713. The vapour from the heated flask passes over into the condenser, where it is cooled by the circulating cold water and turns back into a liquid, which is collected in the receiver. If necessary, to reduce thermal decomposition, the process can be carried out at a lower temperature by reducing the pressure in the apparatus so as to reduce the boiling point of the liquid (refer to Figure 711).

A mixture of two miscible, volatile liquids, will boil when the sum of the vapour pressures of the two components equals the external pressure. The vapour will always contain a greater proportion of the more volatile component than the liquid phase does. If the liquid contains an equal number of moles of two liquids, at the boiling point of the mixture, the more volatile component will be contributing more than 50% of the vapour pressure. For example the vapour above an equimolar mixture of benzene (b.p. = 353 K) and methylbenzene (b.p. = 384 K) will contain more than 50% benzene, but it is not possible to obtain pure benzene by simple distillation as there would still be significant amounts of methylbenzene vapour. Such a mixture could however be more completely separated by successive distillations – the greater the difference in boiling points the easier the separation.

Returning to the equimolar mixture of benzene and methylbenzene, the vapour pressures of the two components over the mixture at various temperatures are shown in Figure 714. At a particular temperature (~ 370 K) the total vapour pressure over the mixture equals atmospheric pressure and the mixture boils. The vapour evolved will contain the two components in the ratio of their vapour pressures at that temperature (~ 70% benzene and ~ 30% methylbenzene).

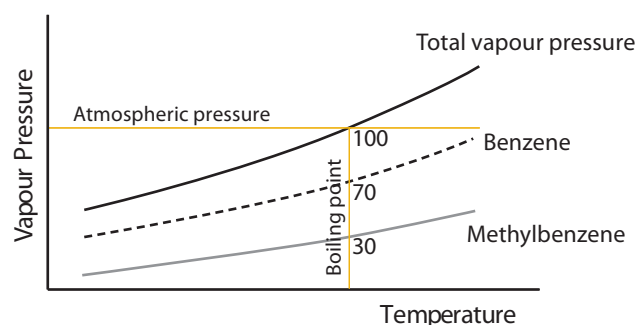


Figure 714 The vapour pressures in an equimolar benzene–methylbenzene mixture

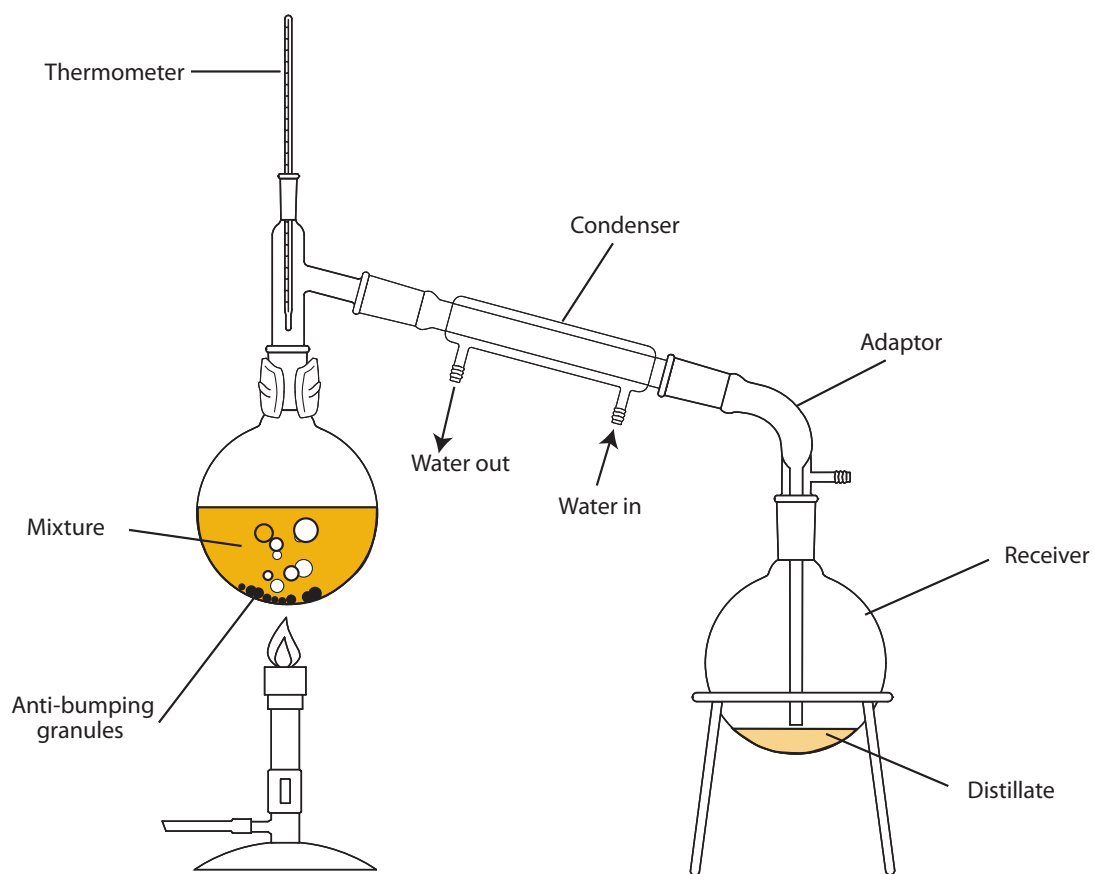


Figure 713 Typical simple distillation apparatus

EXTENSION

If this 70-30 mixture is now distilled, it will boil at a lower temperature ( $\sim 365$  K), as it is richer in the more volatile component, and the vapour that distils off will be even richer in benzene ( $\sim 85\%$  benzene and  $\sim 15\%$  methylbenzene). This can again be distilled giving a product still richer in benzene and this process can be continued until the required degree of purity is obtained. This is best illustrated in the form of a boiling point composition graph for the system, shown in Figure 715, which indicates the boiling point of mixtures of differing compositions (liquid curve) and the composition of the vapour that will distil from this (vapour curve). The result of successive distillations can be seen by drawing lines (sometimes called 'tie lines') parallel to the axes, as shown in Figure 715:

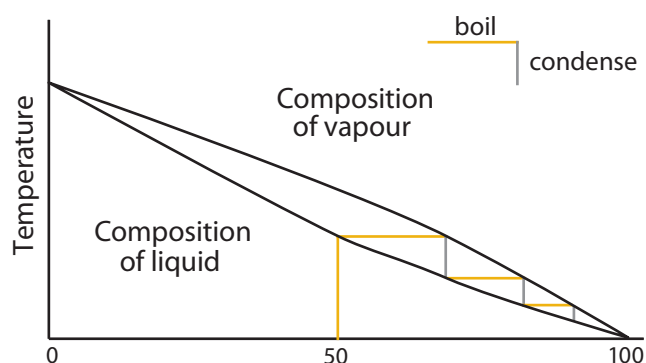


Figure 715 The boiling point–composition graph for benzene-methylbenzene mixtures

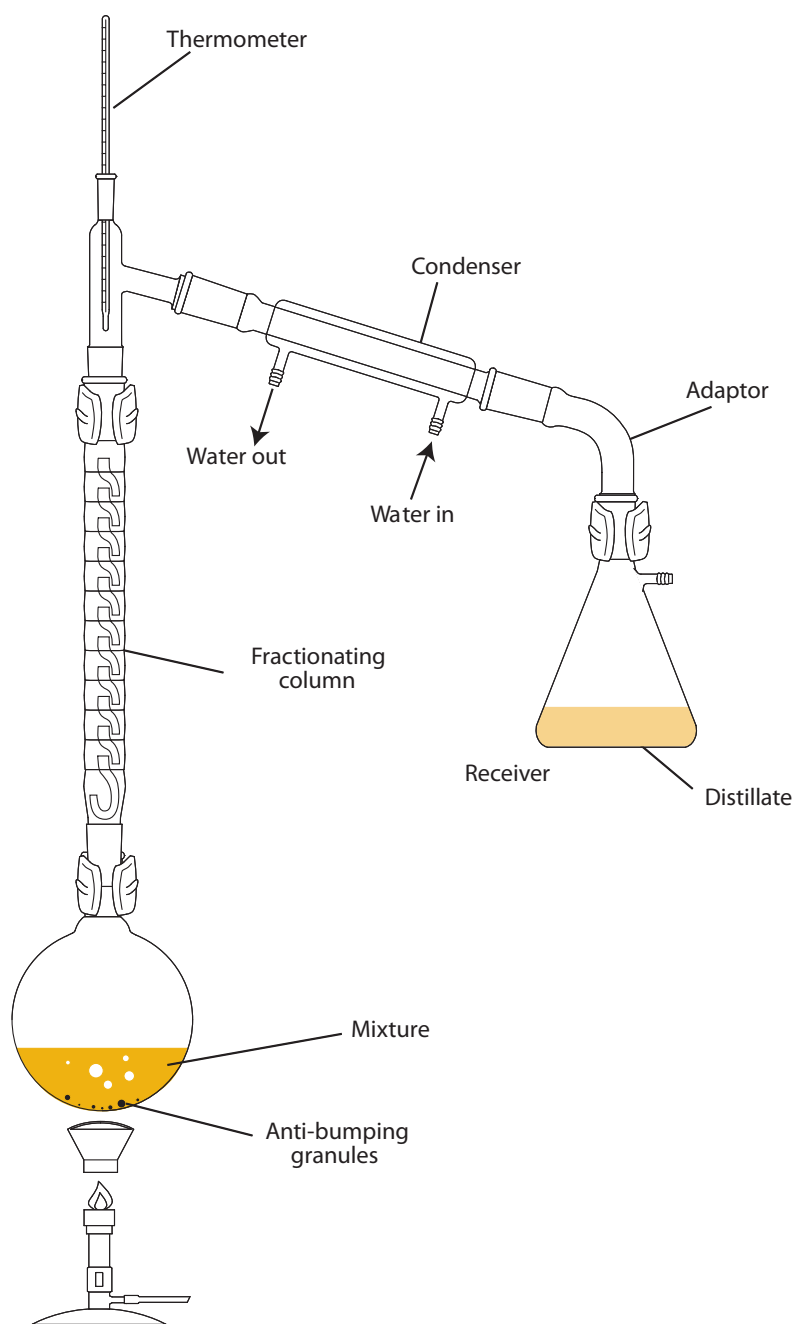


Figure 716 Typical fractional distillation apparatus

In **fractional distillation**, the vapour from the boiling liquid rises up the fractionating column, cools and condenses. It then runs down the column and meets hot vapours rising up, causing it to boil again. Thus as it rises up the column the liquid undergoes a number of vapourisation–condensation–vapourisation cycles, equivalent to having been distilled a number of times – the longer the column the more distillations. If a suitable

column is used, the liquid distilling over will be a pure sample of the more volatile component of the mixture and eventually, in theory, the distillation flask will contain the less volatile component. Fractional distillation is carried out using apparatus similar to that shown in Figure 716. Fractional distillation is used in many industrial processes such as the separation of liquid air and of petroleum (refer to Chapter 14).

## RAOULT'S LAW AND DEVIATIONS FROM IDEALITY

The vapour pressure above a mixture of two miscible liquids is predicted by **Raoult's law**. This assumes that the forces between particles of the two components in the mixture (A–B forces) are identical to those present in the pure components (A–A and B–B forces), hence the vapour pressure of component A over the mixture ( $P_A$ ) is equal to the vapour pressure of the pure component  $P_A^0$  multiplied by its mole fraction:

$$P_A = P_A^0 \times \frac{\text{moles of A}}{\text{total moles}}$$

In many cases when the molecules only have weak van der Waals' forces between them, such as the cases of benzene and methylbenzene above, the situation approximates well to this ideal behaviour and the total vapour pressure varies in a linear manner with composition (see a in Figure 717). In other cases only minor deviations from ideality occur and the vapour pressure/composition graph is a smooth curve (see b in Figure 717). In some cases however, where strong inter-particle forces occur, as a result of hydrogen bonding or dissociation of one of the species, there are major deviations from ideality.

If the inter-particle forces in the mixture are weaker than those in the pure liquids, then it is easier for the particles to escape from the mixture, increasing the vapour pressure above the value predicted by Raoult's law (a positive deviation from Raoult's Law). In extreme cases of a **positive deviation from Raoult's Law**, the vapour pressure/composition graph will pass through a maximum, and as a result the boiling point/composition diagram will pass through a minimum (see c in Figure 717). In such cases separation of both components by fractional distillation is not possible because the liquid that distils over is not a pure component, but the mixture with the minimum boiling point. The mixture with this composition is known as an **azeotrope**. An example of this type of behaviour is a mixture of ethanol and water, where the azeotropic mixture (96% ethanol, 4% water) boils at a temperature of 78.2 °C, whereas the boiling point of pure ethanol is 78.5 °C.

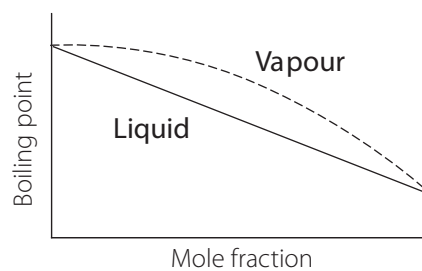
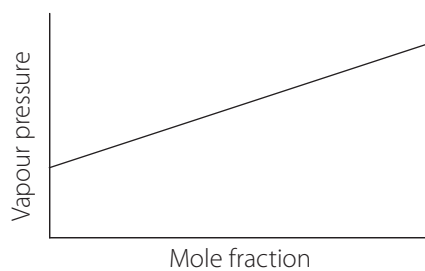
If the inter-particle forces in the mixture are stronger than those in the pure liquids, then it is more difficult for the particles to escape from the mixture, decreasing the vapour pressure below the value predicted by Raoult's law (a negative deviation). In extreme cases of a **negative deviation from Raoult's Law** the vapour pressure/composition graph will pass through a minimum, and as

a result the boiling point/composition diagram will pass through a maximum (see d in Figure 717). Again it is not possible to separate the mixture into the two components because the liquid that remains in the flask is the mixture with the maximum boiling point. This mixture is also known as an azeotrope. An example of this type of behaviour is a mixture of nitric acid and water, where the azeotropic mixture (68% nitric acid, 32% water) boils at a temperature of 121 °C, whereas the boiling point of pure nitric acid is 83 °C.

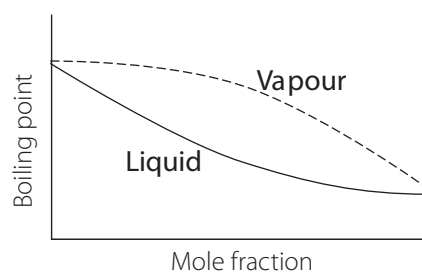
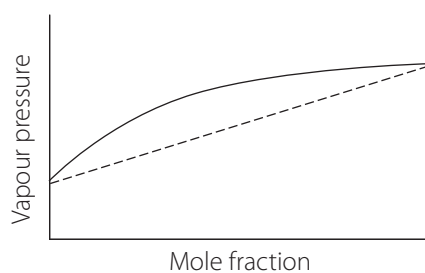
### Exercise

- As the temperature increases, the vapour pressure of a liquid increases because
  - the intermolecular forces become weaker.
  - expansion causes the surface area of the liquid to increase.
  - a greater proportion of the molecules have the kinetic energy required to escape from the surface.
  - the number of molecules in the gas phase is constant, but they are moving at a greater velocity.
- At 50 °C, which one of the following liquids would you expect to have the greatest vapour pressure?
  - Ethanol
  - Lubricating oil
  - Mercury
  - Water
- Which one of the following does not affect the boiling point of a liquid?
  - The strength of the intermolecular forces.
  - Its surface area.
  - The external pressure.
  - The presence of dissolved impurities.

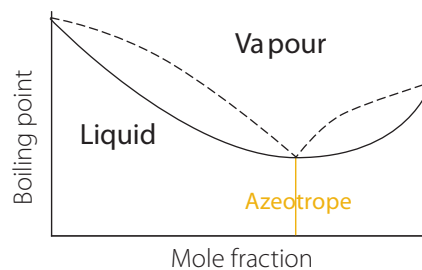
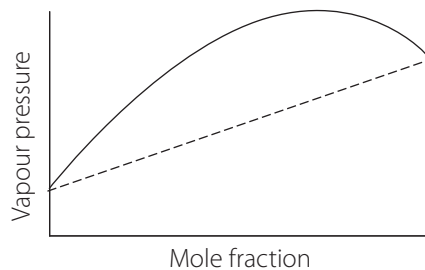
a) An ideal mixture



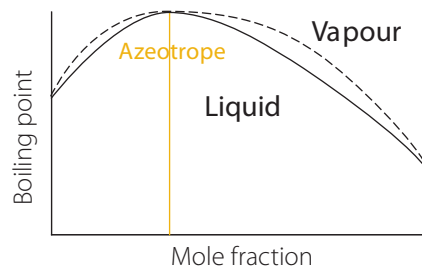
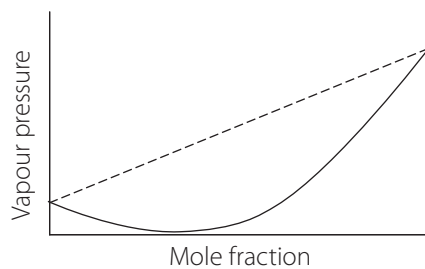
b) A slight positive deviation from Raoult's law



c) A major positive deviation from Raoult's law (e.g. ethanol-water)



d) A major negative deviation from Raoult's law (e.g. nitric acid-water)



EXTENSION

Figure 717 a, b, c, d Vapour pressure/composition and boiling point/composition graphs for ideal and non-ideal solutions

4. A mixture containing equal numbers of moles of hexane (b.p. 69 °C) and cyclohexane (b.p. 81 °C) is heated.
- What conditions determine the temperature at which the liquid boils?
  - What do the boiling points show about the relative strengths of the intermolecular forces in the two components?
  - Would you expect this mixture to boil below 69 °C, between 69 °C and 81 °C, or above 81 °C? Explain why.
  - How would you expect the composition of the vapour to compare with that of the liquid? Explain why this is so.
  - If the vapour is condensed and then further distilled a number of times, what will happen to the proportions of the two components in the distillate?
  - What separation technique depends on this principle?
  - Give one industrial application of this separation method.

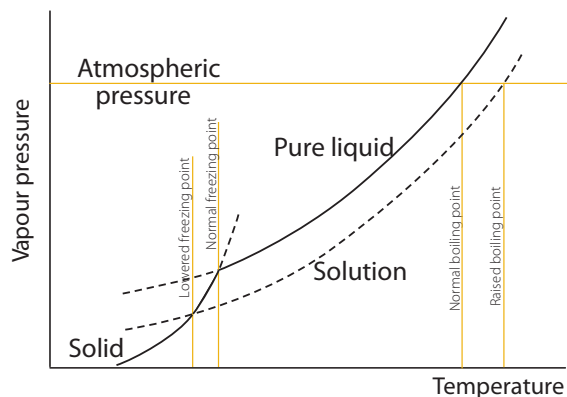


Figure 718 The effect of a non-volatile solute on freezing point and boiling point

An alternative explanation depends on the fact that when one phase is in equilibrium with another  $\Delta G = 0$ , that is,  $\Delta H = T\Delta S$ . Adding the non-volatile solute to the liquid phase increases the entropy of the liquid phase without affecting that of either the solid or vapour. This decreases  $\Delta S$  for the phase change into the vapour (as the vapour has a greater entropy than the liquid  $\Delta S = S_{\text{vap}} - S_{\text{liq}}$  gets smaller), hence a greater temperature is required for  $T\Delta S$  to equal  $\Delta H$ . It will however increase  $\Delta S$  for the phase change from solid to liquid (in this case the solid has a lower entropy than the liquid so  $\Delta S = S_{\text{liq}} - S_{\text{sol}}$  gets greater), so that it requires a lower temperature for  $T\Delta S$  to equal  $\Delta H$ .

## COLLIGATIVE PROPERTIES OF SOLUTIONS

### EXTENSION

As was discussed previously (Section 7.4), the addition of a non-volatile solute to a solvent lowers its vapour pressure and this will affect both its **freezing point** and its **boiling point**. As a liquid boils when its vapour pressure is equal to the external pressure, by lowering the vapour pressure, a solute will increase the temperature required for this to occur, that is it elevates the boiling point, as shown in Figure 718.

At the freezing point of a substance the vapour pressure of both the liquid and the solid states must be equal. If this were not the case then, if both the liquid and solid were placed in an evacuated container at the freezing point, equilibrium would not exist. Normally when a solution freezes it is the pure solvent that separates from the solution, leaving the solute in the liquid phase. This means the vapour pressure of the solid state is unaffected, so lowering the vapour pressure of the liquid state means that it is not equal to that of the solid until a lower temperature, that is it depresses (lowers) the freezing point, as shown in Figure 718.

The decrease in the vapour pressure of a particular solvent is proportional to the concentration of solute particles because they occupy spaces on the surface and hence reduce the surface available for solvent molecules to escape from. It is the concentration of such particles rather than the nature of the particles that is important, as a result in aqueous solution one mole of sodium chloride (which dissociates into  $\text{Na}^+$  and  $\text{Cl}^-$ ) will have twice the effect of one mole of sucrose (which does not dissociate) and aluminium sulfate will have five times the effect ( $2 \times \text{Al}^{3+}$  and  $3 \times \text{SO}_4^{2-}$ ). The magnitude of the effect varies from solvent to solvent, dependent mainly on its molar mass, but constants (**cryoscopic constants** for freezing and **ebullioscopic constants** for boiling) have been measured for most common solvents. These usually give the change in boiling/freezing point when one mole of particles is dissolved in 1 kg of the solvent, and if this is the case, the change in boiling/freezing point can be calculated using the formula:

$$\Delta T = K \times \frac{n \times m_{st}}{M_{st}} \times \frac{1000}{m_{sv}}$$

Where  $K$  is the relevant constant (units  $\text{K mol}^{-1} \text{ kg}$ ),  $n$  the number of particles the solute dissociates into,  $m_{st}$  the mass of the solute,  $m_{sv}$  the mass of the solvent (both masses in g) and  $M_{st}$  the molar mass of the solute.

## Example

The freezing point depression constant for water is  $1.86 \text{ K mol}^{-1} \text{ kg}$ . By how much will dissolving 5.00 g of sodium chloride in 100 g of water lower the freezing point?

## Solution

$$\begin{aligned}\Delta T &= K \times \frac{n \times m_{st}}{M_{st}} \times \frac{1000}{m_{sv}} \\ &= 1.86 \times \frac{2 \times 5.00}{58.5} \times \frac{1000}{100} \\ &= 3.18 \text{ K}\end{aligned}$$

Because their magnitude is proportional to the number of moles of solute particles and is not dependent on the nature of these particles, reduction in vapour pressure, elevation of boiling point and depression of freezing point are all known as **colligative properties** of solutions. One other property that also varies in this way, and hence is also counted as a colligative property, is the **osmotic pressure** of a solution, discussed below. In all cases, the direct proportionality to the concentration of solute particles is only an approximation, the accuracy of which decreases as the concentration increases.

If a solvent and a solution are separated by a selectively permeable membrane (one that allows solvent molecules to pass through, but not solute particles) then, if the pressure on both sides of the membrane is equal, the rate at which solvent molecules pass into the solution will be greater than the rate at which they pass out of it. This is because on the solution side, some of the collisions between particles and the membrane involve solute particles that cannot pass through (making the pressure of the solvent less than the total pressure), whereas on the solvent side the pressure is totally generated by the collision of solvent molecules. The result is the net transfer of solvent molecules from the pure solvent to the solution – a process known as **osmosis**. The system may be brought into equilibrium and the transfer of solvent stopped by applying additional pressure to the solution side. The additional pressure required is known as the **osmotic pressure**. This is illustrated in Figure 719:

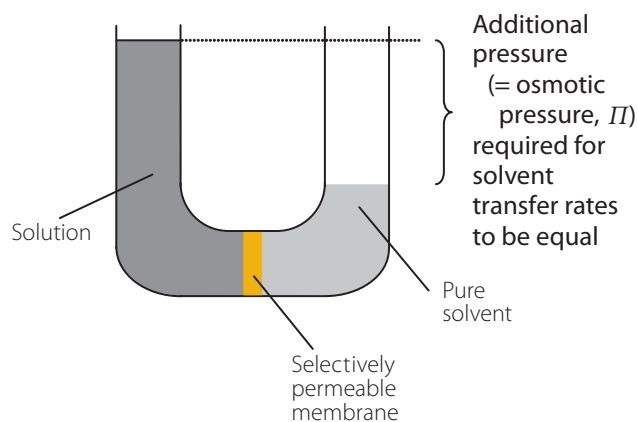


Figure 719 Osmotic pressure

The osmotic pressure of a solution may be calculated from the expression:

$$\Pi V = nRT$$

Where  $\Pi$  is the osmotic pressure in kPa,  $V$  the volume of solvent in  $\text{dm}^3$ ,  $n$  the number of moles of solute particles,  $R$  the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $T$  the absolute temperature.

## Example

What is the osmotic pressure of a solution of 2.64 g of ammonium sulfate in  $250 \text{ cm}^3$  of water at 300 K?

## Solution

$$\begin{aligned}\text{Amount of ammonium sulfate} &= \frac{m}{M} \\ &= \frac{2.64}{132} \\ &= 0.0200 \text{ moles}\end{aligned}$$

$$\begin{aligned}\text{Amount of solute particles} &= 3 \times 0.0200 \\ &= 0.0600 \text{ moles}\end{aligned}$$

(as  $(\text{NH}_4)_2\text{SO}_4$  dissociates into  $2 \times \text{NH}_4^+$  and  $1 \times \text{SO}_4^{2-}$ )

$$\begin{aligned}\Pi &= \frac{nRT}{V} \\ &= \frac{0.0600 \times 8.314 \times 300}{0.250} \\ &= 599 \text{ kPa (nearly six times atmospheric pressure!)}\end{aligned}$$

Historically all of the colligative properties were important ways of determining the molar mass of a substance.

### Example

When 1.00 g of a natural oil is dissolved in 50.0 g of tetrachloromethane (boiling point elevation constant  $5.02 \text{ K mol}^{-1} \text{ kg}$ ), the boiling point is increased by  $0.500^\circ\text{C}$ .

### Solution

$$\begin{aligned}\Delta T &= K \times \frac{n \times m_{st}}{M_{st}} \times \frac{1000}{m_{sv}} \\ &= 5.02 \times \frac{1 \times 1.00}{M_{st}} \times \frac{1000}{50} \\ &= 0.500\end{aligned}$$

$$\begin{aligned}M_{st} &= 5.02 \times \frac{1 \times 1.00}{0.500} \times \frac{1000}{50} \\ &= 200.8 \text{ g mol}^{-1}\end{aligned}$$

### Exercise

- Which one of the following is not a colligative property of a solution?
  - Vapour pressure
  - Elevation of boiling point
  - Depression of freezing point
  - Osmotic pressure
- Which of the following will have approximately the same effect on the freezing point of water as 0.1 mole of sodium chloride?
  - 0.3 mole of sodium sulfate
  - 0.1 mole of glucose
  - 0.1 mole of copper(II) nitrate
  - 0.05 mole of aluminium chloride
- When 1.50 g of naphthalene is dissolved in 50.0 g of cyclohexane (freezing point depression constant  $20.1 \text{ K mol}^{-1} \text{ kg}$ ), the freezing point is decreased by  $4.70^\circ\text{C}$ . What is the molar mass of naphthalene?
- When 0.0135 moles of a non-volatile solute is added to 20.0 g of a solvent in which it does not dissociate, the boiling point of the solvent increases by  $1.20^\circ\text{C}$ . Calculate the ebullioscopic constant of the solvent, giving appropriate units.

- When 5.00 g of a non-volatile solute of molar mass  $150 \text{ g mol}^{-1}$  is dissolved in  $500 \text{ cm}^3$  of water at  $25.0^\circ\text{C}$ , the osmotic pressure is found to be 330 kPa. What can you deduce about the substance from this information?

## OTHER EQUILIBRIUM CONSTANTS

### In terms of partial pressures – $K_p$

The concentration of a gas is proportional to its **partial pressure** and it is sometime more convenient to write the equilibrium constant for a gas phase equilibrium in terms of this. This equilibrium constant is differentiated from that in terms of concentration by using the subscript 'p' rather than the subscript 'c'. Therefore for a general equilibrium



in which all the components are in the gas phase, the equilibrium constant in terms of partial pressures is given by

$$K_p = \frac{p(\text{S})^s p(\text{T})^t p(\text{U})^u \dots}{p(\text{A})^a p(\text{B})^b p(\text{C})^c \dots}$$

Where  $p(\text{A})$  represents the partial pressure of A, which can be calculated from the total pressure ( $P_{\text{tot}}$ ) and the amount of A in the mixture using the expression:

$$p(\text{A}) = P_{\text{tot}} \times \frac{\text{moles of A}}{\text{total moles}}$$

For example in the equilibrium between ammonia and oxygen to give nitrogen monoxide and steam:



The equilibrium constant is given by

$$K_p = \frac{p(\text{NO})^4 p(\text{H}_2\text{O})^6}{p(\text{NH}_3)^4 p(\text{O}_2)^5} \text{ Kpa}$$

As with  $K_c$ ,  $K_p$  does not have fixed units and they must be calculated in each case.

The concentration of a gas is linked to its partial pressure using the ideal gas equation:

$$[\text{A}] = \frac{n_a}{v} = \frac{p(\text{A})}{RT}$$

This relationship can be used to inter-convert  $K_p$  and  $K_c$  values, by substituting in the relevant equation. This leads to  $K_p = K_c (RT)^{\Delta n}$  where  $\Delta n$  is the change in the number of moles of gas.

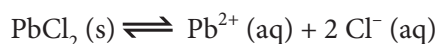
It will have been noted by many students that the equilibrium constant and the free energy change for a reaction ( $\Delta G$ ) are both measures of the extent to which the reactants are converted to the products in a chemical reaction at equilibrium. It is not surprising therefore that the two quantities are linked. The exact relationship is:

$$\Delta G^\circ = -RT \ln K_p$$

## The solubility product – $K_{sp}$

[EXTENSION, but note that though not required in the Core or AHL sections of the IB syllabus, the solubility product is referred to in Section E12 of the Environmental Chemistry option, see Chapter 16.]

The **solubility product** is the name given to the equilibrium constant ( $K$ ) for an ionic solid in equilibrium with its aqueous ions (remembering that the concentrations of solids are omitted from such expressions). For example for a saturated solution of lead(II) chloride, the equilibrium and the solubility product is:



$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \text{ mol}^3 \text{ dm}^{-9}$$

It is really only a useful concept for sparingly soluble electrolytes as concentrated ionic solutions exhibit significant deviations from ideal behaviour. The solubility product can be calculated from the solubility of a substance and vice versa.

### Example

The solubility of lead(II) chloride at 298 K is  $3.90 \times 10^{-4} \text{ mol dm}^{-3}$ , what is the solubility product for lead(II) chloride at this temperature?

### Solution

From the equation above, each formula unit of lead(II) chloride forms one lead ion and two chloride ions, therefore:

$$\begin{aligned} [\text{Pb}^{2+}] &= 3.90 \times 10^{-4} \text{ mol dm}^{-3} \text{ and} \\ [\text{Cl}^{-}] &= 2 \times 3.90 \times 10^{-4} \\ &= 7.80 \times 10^{-4} \text{ mol dm}^{-3}; \end{aligned}$$

substituting:

$$\begin{aligned} K_{sp} &= [\text{Pb}^{2+}] \times [\text{Cl}^{-}]^2 \\ &= 3.90 \times 10^{-4} \times (7.80 \times 10^{-4})^2 \\ &= 2.37 \times 10^{-10} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

Ions behave independently in solution and hence, in the above example, the chloride ions need not necessarily come from the lead(II) chloride, they could also come from some other solute, for example hydrochloric acid. This means that an ionic solid is significantly less soluble in a solution that already contains one of its component ions, than it is in pure water. This is known as the **common ion effect**.

### Example

Calculate the solubility of lead(II) chloride, in  $\text{g dm}^{-3}$ , in  $0.100 \text{ mol dm}^{-3}$  hydrochloric acid at 298 K, given its solubility product determined above.

### Solution

$[\text{Cl}^{-}] = 0.100 \text{ mol dm}^{-3}$ , (assuming any ions from the lead(II) chloride are negligible), therefore

$$\begin{aligned} K_{sp} &= [\text{Pb}^{2+}] \times [\text{Cl}^{-}]^2 \\ &= [\text{Pb}^{2+}] \times (0.1)^2 \\ &= (2.37 \times 10^{-10} \text{ mol}^3 \text{ dm}^{-9}) \end{aligned}$$

$$\begin{aligned} [\text{Pb}^{2+}] &= \frac{2.37 \times 10^{-10}}{0.0100} \\ &= 2.37 \times 10^{-8} \text{ mol dm}^{-3} \end{aligned}$$

$$= [\text{PbCl}_2] \text{ (note this is much less than in water)}$$

$$M_r(\text{PbCl}_2) = 278$$

$$\begin{aligned} m &= n \times M_r \\ &= 2.37 \times 10^{-8} \times 278 \\ &= 6.60 \times 10^{-6} \text{ g dm}^{-3} \end{aligned}$$

The solubility product may be used to predict whether a sparingly soluble salt will be precipitated under particular circumstances. The concentrations of the ions that would be present is calculated and then substituted into

the solubility product expression. If the result of this is greater than the solubility product, then the solid will be precipitated.

### Example

The solubility product for silver sulfate is  $1.60 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$ . Would silver sulfate be precipitated when  $20.0 \text{ cm}^3$  of  $0.0100 \text{ mol dm}^{-3}$  aqueous silver nitrate is mixed with  $30.0 \text{ cm}^3$  of  $2.00 \text{ mol dm}^{-3}$  sulfuric acid?

### Solution

$$[\text{Ag}^+] = 0.01 \times \frac{20.0}{50.0}$$

$$= 0.004 \text{ mol dm}^{-3};$$

$$[\text{SO}_4^{2-}] = 2.00 \times \frac{30.0}{50.0}$$

$$= 1.20 \text{ mol dm}^{-3}$$

(Note the allowance made for the dilution effect of mixing solutions);

substituting:

$$K_{sp} = [\text{Ag}^+]^2 \times [\text{SO}_4^{2-}]$$

$$= (0.00400)^2 \times 1.20$$

$$= 1.92 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

This is just greater than the solubility product ( $1.60 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$ ), so a small quantity of solid silver sulfate would be precipitated.

### Exercise

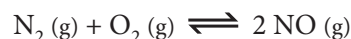
1. For which one of the following would  $K_p$  and  $K_c$  have the same numerical value at the same temperature?

- A  $2 \text{ SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons 2 \text{ SO}_3 (\text{g})$   
 B  $\text{C} (\text{s}) + \text{H}_2\text{O} (\text{g}) \rightleftharpoons \text{CO} (\text{g}) + \text{H}_2 (\text{g})$   
 C  $\text{N}_2 (\text{g}) + 3 \text{ H}_2 (\text{g}) \rightleftharpoons 2 \text{ NH}_3 (\text{g})$   
 D  $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \rightleftharpoons 2 \text{ HI} (\text{g})$

2. In which of the following solutions will silver chloride be least soluble?

- A  $0.1 \text{ mol dm}^{-3}$  sodium chloride  
 B  $0.1 \text{ mol dm}^{-3}$  glucose  
 C  $0.1 \text{ mol dm}^{-3}$  copper(II) nitrate  
 D  $0.1 \text{ mol dm}^{-3}$  aluminium chloride

3. When air (assume 20% oxygen, 80% nitrogen) is heated to 2000 K at a pressure of 100 kPa, 3.0% of the oxygen is converted to nitrogen monoxide in the equilibrium:



Calculate the partial pressures of  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{NO}$  at equilibrium.

4. The solubility of calcium sulfate is  $6.34 \text{ g dm}^{-3}$ .

- a) Calculate its solubility product, stating the units.  
 b) If equal volumes of  $0.1 \text{ mol dm}^{-3}$  solutions of calcium chloride and sulfuric acid are mixed would you expect a precipitate of calcium sulfate to form. Explain your reasoning.

5. The solubility product of magnesium hydroxide is  $2.0 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$ .

- a) Calculate its solubility in  $\text{g dm}^{-3}$ .  
 b) What is the concentration of hydroxide ions in a saturated solution?  
 c) How many grams of the solid would dissolve in  $50 \text{ cm}^3$  of water?  
 d) How many grams would dissolve in  $50 \text{ cm}^3$  of  $0.010 \text{ mol dm}^{-3}$  aqueous sodium hydroxide?  
 e) Explain why the two values differ.

6. The solubility products of zinc carbonate and zinc hydroxide are:

$$1.4 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6} \text{ and}$$

$$2.0 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-9} \text{ respectively.}$$

- a) Write chemical equations, including state symbols, for the two equations involved.  
 b) Write solubility product expressions for these.  
 c) Saturated aqueous solutions are made of these compounds. Which has the higher concentration of zinc ions?  
 d) A solution containing zinc ions is added to a solution that is  $0.10 \text{ mol dm}^{-3}$  in both hydroxide and carbonate ions. Which solid will precipitate out first and what concentration of zinc ions would be required for this to occur? (Assume negligible change in total volume.)