

Equilibrium and Le Châtelier's Principle

To succeed in this topic you need to:-

- be able to write balanced chemical equations.

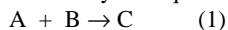
After working through this Factsheet, you will understand:-

- the terms 'reversible' and 'irreversible' reactions.
- the meaning of dynamic equilibrium.
- the working and effects of dynamic equilibrium.
- Le Châtelier's Principle.
- the effect of change of conditions on position of equilibrium.
- the Haber Process (production of ammonia).
- the Contact Process (production of sulphuric acid).

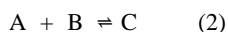
Exam Hint: Questions on the effect of change of conditions on position of equilibrium are common. Knowledge of industrial processes is often tested – so the Chemistry behind them needs to be learnt. candidates must be aware of the need for 'optimum conditions and 'maximum efficiency' in industry for financial reasons.


Many reactions are **irreversible**, which means that they move in one direction only. One common example of this is burning an item - it is easy to burn something, but you cannot reassemble the original item from the ashes!

If A and B react completely to form product C, the reaction can be represented by the equation.



There are also many reactions, which are **reversible** - that is to say that they can proceed in both directions. For example, if A and B react to form C, and C can also decompose to form A and B, this can be represented by the equation:



 → means irreversible (or 'one-way') reaction
⇌ means reversible (or 'two-way') reaction

In reaction (1) there is a **total conversion** of reactants A and B to product C. In reaction (2) there will always be a mixture of reactants and products as forward and backward reactions continue constantly.

Reversible reactions naturally reach a point when the rate of the forward reaction equals the rate of the backward reaction - this is known as **equilibrium**.

Equilibrium

Equilibrium is a state of balance. There are 2 types of equilibrium:-

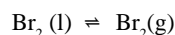
1. Dynamic Equilibrium.
2. Static Equilibrium.

In static equilibrium, nothing is happening - no changes are occurring. A book lying on a table is an example of this! You may have met examples of this in other subjects. In Chemistry, we always work with **dynamic equilibrium**.

Dynamic Equilibrium

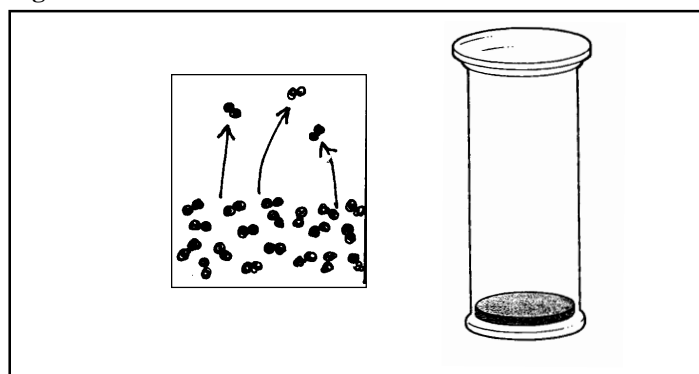
Consider a café on a busy afternoon – all 40 seats in the café are occupied for the whole afternoon. People are coming and going all the time – some stay for long periods, some only a short while, but the population remains constant at 40 people. There is obviously a balance between the number leaving and the number arriving. This state of balance is an equilibrium - and it is dynamic because the people are changing. (If the same 40 people sat there, it would be static equilibrium).

We must now look at dynamic equilibrium on the scale of particles. Consider placing 5cm³ of the volatile liquid bromine into a gas jar. At room temperature some of the molecules in the liquid have enough energy to form vapour, meanwhile some of the molecules in the vapour have too little energy so move back into the liquid phase. Hence we have a reversible reaction.



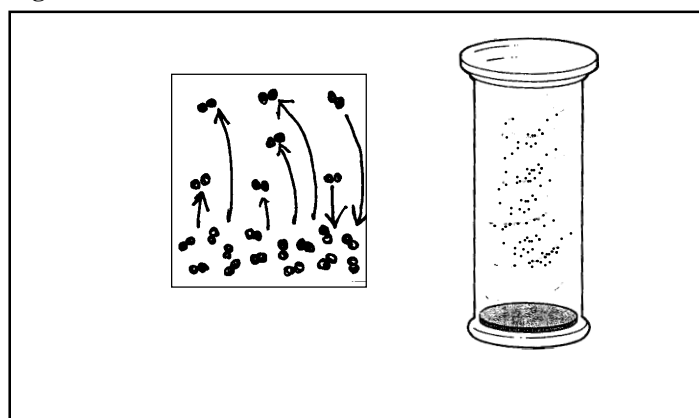
On adding liquid bromine to an empty gas jar, there is no equilibrium initially, as vaporisation is taking place, but no condensation (Fig 1).

Fig 1.



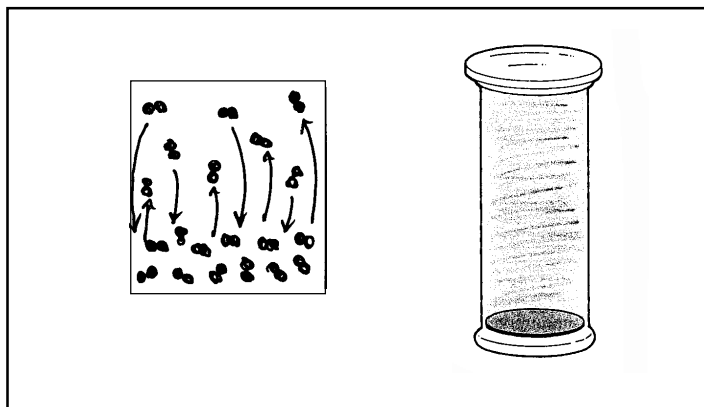
After 2 minutes, the brown vapour can be seen clearly, and it is getting more dense. The level of the liquid bromine is going down. The rate of vaporisation is higher than the rate of condensation – so equilibrium has not been reached (fig 2).

Fig 2.



After 30 minutes a thick brown vapour can be seen and liquid is still present. The vapour is no longer getting denser and the level of the liquid is unchanging (Fig 3).

Fig 3.



Rate of vaporisation = Rate of condensation

Therefore a dynamic equilibrium has been reached.

Dynamic equilibrium in reversible reactions

All reversible reactions reach a state of dynamic equilibrium.

This means that they reach a state where the amount of products present and the amount of reactants present does not change.

At equilibrium:

- Despite there being no apparent change, both forward and reverse processes continue.
- Rate of forward reaction is equal to rate of reverse reaction.
- Concentrations of reactions and products remain constant.

Equilibrium can be attained from either forward or reverse directions. In other words, it does not matter whether you start from the reactants or the products - you will still end up with the **same** equilibrium position.

Equilibrium can only be attained in a **closed system** - this means one in which reactants and products are not added or removed.

Position of equilibrium

At equilibrium, we know we will have a mixture of reactants and products - but we need to know **how much** of each there is - this is what is meant by the **position of equilibrium**. For example, does the equilibrium mixture contain more reactant than product, or vice versa?

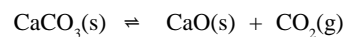
Remember: The rates of the forward and backward reactions are equal at equilibrium, but this tells us **nothing** about the amounts (or concentrations) of products and reactants. The **concentrations** of the reactants and products will be **different** at equilibrium.

- If the equilibrium mixture contains more products than reactants, we say **the forward reaction is favoured**.
- If it contains more reactants than products, we say **the reverse reaction is favoured**.

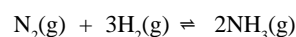
The position of the equilibrium is affected by changing conditions such as temperature, pressure and concentration of reactants/products; the next section explains how this works.

Examples of equilibria in chemical reactions

1. If calcium carbonate is heated in a closed container, at first it decomposes to calcium oxide and carbon dioxide faster than the products can recombine. After a while, the levels of calcium oxide and carbon dioxide are built up to a level at which the rate of recombination of these products is equal to the rate of decomposition of calcium carbonate. The system reaches a state of dynamic equilibrium:



2. Nitrogen and hydrogen gases combine to form ammonia. Ammonia decomposes to form nitrogen and hydrogen. In a closed system a dynamic equilibrium is reached where the rate of combination is equal to the rate of decomposition:



Effect of Change of Conditions on Position of Equilibrium.



Le Châtelier's Principle

If a system in dynamic equilibrium is subjected to a change, processes will occur to counteract this change and to restore equilibrium.

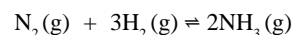
In other words, the equilibrium will "attempt to undo any change" - so if you increase the pressure, it will "try" to lower it etc. This will alter the amount of reactants and products present in the equilibrium mixture, as explained below. We will consider the effect on the equilibrium position of changing:-

- concentrations
- pressure
- temperature
- catalyst

Table 1 overleaf summarises the effect of all these changes.

The Effect of Changing Concentrations

Consider the reaction:-



At equilibrium concentration of reactants and products remain constant. If more $\text{N}_2(\text{g})$ is introduced into the closed system the system tries to **counteract** this change and reduce the concentration of $\text{N}_2(\text{g})$. It does this by moving the equilibrium to the right - to "use up" some of the $\text{N}_2(\text{g})$ in producing more $\text{NH}_3(\text{g})$.

If some $\text{N}_2(\text{g})$ was removed from the system, then the system would counter this by moving the equilibrium to produce more of it - thus shifting the equilibrium to the left.

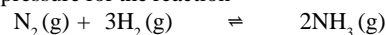
The Effect of Changing Pressure

Pressure changes **only** affect equilibrium when a **gas** is present.

- Increasing the number of gas molecules present in a closed system will increase pressure.
- Decreasing the number of gas molecules will decrease pressure.

If the pressure of a system is increased, then the system counteracts this by moving the position of equilibrium to reduce it. This means that the equilibrium moves towards the side with fewer gas molecules. If the pressure is decreased, then this is counteracted by the equilibrium moving towards the side with more gas molecules.

eg. Increasing pressure for the reaction

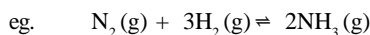


will cause equilibrium to move to the right, since there are 2 gas molecules on that side, but 4 on the left.

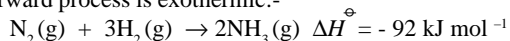
NB: If the number of gas molecules on each side is the same, then pressure changes have no effect.

The Effects of Changing Temperature

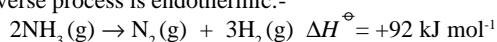
The **energy changes** involved in reversible reactions are **equal** and **opposite**. This means that in one direction an **exothermic** reaction occurs and in the other an **endothermic** reaction.



The forward process is exothermic:-



The reverse process is endothermic:-



If the temperature of the system in equilibrium is decreased, the equilibrium will move to counteract this change by releasing heat energy – hence the exothermic reaction would be favoured and equilibrium moves to the right.

If the temperature was increased, then the system would act to reduce it, by favouring the endothermic reaction - hence the equilibrium would move to the left.

The Effects of Catalysts

Adding a catalyst will have **no effect** on the position of equilibrium – but as the rates of both forward and reverse reactions is increased, equilibrium may be reached more quickly.

Table 1. The effects of various factors on equilibrium position

Factor	Effects on equilibrium position
Concentration	\uparrow conc. of reactants \Rightarrow moves to right \downarrow conc. of reactants \Rightarrow moves to left \uparrow conc. of products \Rightarrow moves to left \downarrow conc. of products \Rightarrow moves to right (remember: move to left means more reactants move to right means more products)
Pressure	\uparrow pressure \Rightarrow moves to side with fewer gas molecules \downarrow pressure \Rightarrow moves to side with more gas molecules <ul style="list-style-type: none"> ▪ Only affects reactions involving gases ▪ Only has an effect if there are different numbers of gas molecules on each side
Temperature	\uparrow temperature \Rightarrow moves in the direction of endothermic reaction (ΔH positive) \downarrow temperature \Rightarrow moves in the direction of exothermic reaction (ΔH negative)
Catalyst	No effect on equilibrium position (but equilibrium attained faster)

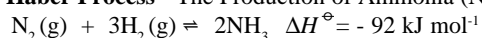
Equilibrium in Industry

In many reactions the final yield of a chemical product can vary considerably depending on what conditions are used – as the position of equilibrium can be affected. In industry, reactions and conditions must be considered carefully to produce the most cost-effective method of making a chemical.

The following points are important:-

- Availability of chemicals required for process.
- Equilibrium conditions needed for a good yield.
- A rate of reaction which is fast, yet does not make the reaction explosive or uncontrollable.
- Safety of workers and environment.

1. The Haber Process - The Production of Ammonia (NH_3)



Raw materials are cheaply available :- nitrogen from the air, and hydrogen from natural methane gas (CH_4) and water (H_2O).

For a high field of ammonia, the equilibrium needs to be moved to the right (favouring the forward reaction) as far as possible. This requires:-

- Low temperature - favouring the exothermic forward reaction.
- High pressure - favouring the forward reaction, as equilibrium shifts to reduce the number of gas molecules present.

However, a very low temperature means a low rate of reaction, which would not be cost effective, and maintaining very high-pressure conditions is both expensive and potentially dangerous. So the process must use a compromise – the optimum conditions:-

- Temperature is picked so that reaction occurs at a realistic rate but the final yield of ammonia is not too low. **450°C** is used
- An **iron catalyst** is introduced to increase reaction rates to equilibrium can be reached quickly.
- A high pressure is used, but one which can be maintained safely, and relatively cheaply. **250 atm** is used

This gives a 15% field of ammonia – low but profit making!

2. The Contact Process - The Production of Sulphuric Acid (H_2SO_4)
 The raw materials are sulphur dioxide (from sulphur being burned in air, or as a by product of metal extraction from sulphides), oxygen from air and water.

When sulphur dioxide and oxygen react, a dynamic equilibrium is reached:
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H^\ominus = -197 \text{ kJ mol}^{-1}$

For this process as high a field of $\text{SO}_3(\text{g})$ as possible is required. The forward reaction will be favoured in the following conditions:-

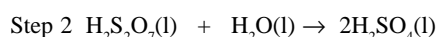
- Low temperature (forward reaction is exothermic).
- High pressure (forward reaction decreases number of gas molecules).

However a very low temperature makes the reaction rate too low and maintaining high-pressure conditions is both expensive and potentially dangerous. So the reaction is carried out using:-

- A temperature of 450°C, where reaction proceeds rapidly and production of SO_3 is still favoured.
- Presence of vanadium(V) oxide catalysts speeds up reactions – so equilibrium is reached faster.
- 1 atm pressure, low (and so cheap and safe) but yield is still high.

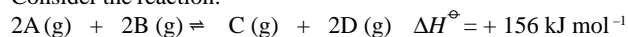
In these conditions, a field of approximately 95% $\text{SO}_3(\text{g})$ is achieved.

The $\text{SO}_3(\text{g})$ must then be converted into sulphuric acid (H_2SO_4). Direct combination of $\text{SO}_3(\text{g})$ with $\text{H}_2\text{O}(\text{l})$ is too dangerous as it is a highly exothermic process, and would vaporise any sulphuric acid formed. Instead $\text{SO}_3(\text{g})$ is reacted with existing $\text{H}_2\text{SO}_4(\text{l})$ to form oleum, $\text{H}_2\text{S}_2\text{O}_7(\text{l})$, which can be converted into the sulphuric acid product safely.



Practice Questions

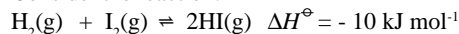
1. Consider the reaction:-



In a closed system, what would be the effect on the position of equilibrium if:-

- The concentration of A was increased?
- The concentration of B was decreased?
- The concentration of C was increased?
- The concentration of D was decreased?
- The pressure on the system was increased?
- The temperature of the system decreased?
- A catalyst was introduced?

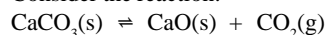
2. Consider the reaction:-



In a closed system, what would be the effect on the position of equilibrium if:-

- The pressure on the system was increased?
- The temperature of the system was increased?

3. Consider the reaction:-



In a closed system, what would be the effect on the position of equilibrium if:-

- An amount of calcium oxide was introduced?
- The pressure on the system was increased?

4. What is meant by the term 'optimum condition' for an industrial process?

5. Explain the following terms:-

- Reversible reaction.
- Dynamic equilibrium.
- Le Châteliers Principle.

Answers

- Equilibrium moves to right.
 - Equilibrium moves to left.
 - Equilibrium moves to left.
 - Equilibrium moves to right.
 - Equilibrium moves to right (reducing number of gas molecules)
 - Equilibrium moves to left (exothermic reaction favoured)
 - No effect on position of equilibrium – but equilibrium may be reached faster as rates of forward and reverse reaction are increased.
- No effect – there are 2 molar molecules of gas molecules on left hand side of equation and 2 molar volumes of gas molecules on right hand side. In this example an increase or decrease in pressure cannot be counteracted by a shift in the position of equilibrium. Consequently an increase in pressure has no effect on the position of equilibrium.
 - Equilibrium moves to left (endothermic process favoured)
- Equilibrium moves to left.
 - Equilibrium moves to left (reducing the number of gas molecules)
- Optimum conditions in an industrial process, one the reaction conditions which produce the required chemical product most cost-effectively and safely. The following must be considered and a compromise worked out.
 - Equilibrium conditions picked to produce high field of product.
 - Rate of reaction must be manageable.
 - Cost of maintaining conditions (pressure, temperature)
 - Safety to workers and environment.
- A reversible reaction is a chemical reaction that can proceed in both directions.
e.g. $A + B \rightleftharpoons C$
 - Dynamic equilibrium in a reversible reaction is where rate of forward reaction = rate of reverse reaction.
Both forward and reverse reactions continues, but because they are proceeding at the same rate, the concentrations of reactions and products remains constant - if pressure is increased, position of equilibrium will move to decrease the number of gas particles (if possible) to reduce the pressure.

If temperature is increased, position of equilibrium will move so the endothermic process is favoured and temperature is decreased.

Acknowledgements:

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