

Application of Rates and Equilibria

Factors effecting equilibrium constants

The effect of various factors (such as temperature and use of a catalyst) on the position of equilibrium can be found in unit 2.

Temperature

In Unit 2 it was seen that by Le Chatelier's principle, increasing the temperature of a reaction causes a shift towards the endothermic reaction. Decreasing the temperature of a reaction causes a shift towards the exothermic reaction.

The explanation for this was seen in the Entropy topic by considering entropy factors in equilibrium reactions.

If the forward reaction is exothermic, an increase in temperature favours the reverse reaction, reducing the quantity of product and increasing the quantity of reactant, so the equilibrium constant is reduced.

If the forward reaction is endothermic, an increase in temperature favours the forward reaction, reducing the quantity of reactant and increasing the quantity of product, so the equilibrium constant is increased.

An increase in temperature always produces an increase in rate. The equilibrium can shift because the proportional increase in rate of the forward and backward reactions will depend upon whether they are endothermic or exothermic.

Pressure

In Unit 2 it was seen that by Le Chatelier's principle, increasing the pressure of a gaseous reaction causes a shift towards the side with fewer molecules. Decreasing the pressure of a gaseous reaction causes a shift towards the side with the larger number of molecules.

The effect of changing pressure on the equilibrium constant can be seen using a hypothetical example: $A \rightleftharpoons D + E$

If A is 20% dissociated at pressure of 1 atm, the value of K_p can be found.

| | A | D | E |
|---------------------|--|--|--|
| Moles - start | 1 | 0 | 0 |
| Moles - equilibrium | 0.8 | 0.2 | 0.2 |
| Partial pressure | $0.8 / 1.2 \times 1$ $= 0.67 \text{ atm}$ | $0.2 / 1.2 \times 1$ $= 0.17 \text{ atm}$ | $0.2 / 1.2 \times 1$ $= 0.17 \text{ atm}$ |

$$K_p = P_B \times P_D / P_A = 0.17 \times 0.17 / 0.67 = 0.0417 \text{ atm}$$

If the pressure is raised the equilibrium would shift to the left. What will this do to the equilibrium constant?

At a pressure of 2 atm the equilibrium shifts to the left so that A is only 14.3% dissociated.

| | A | D | E |
|---------------------|---|--|--|
| Moles - start | 1 | 0 | 0 |
| Moles - equilibrium | 0.857 | 0.143 | 0.143 |
| Partial pressure | $0.857 / 1.143 \times 2$ $= 1.5 \text{ atm}$ | $0.143 / 1.143 \times 2$ $= 0.25 \text{ atm}$ | $0.143 / 1.143 \times 2$ $= 0.25 \text{ atm}$ |

$$K_p = P_B \times P_D / P_A = 0.25 \times 0.25 / 1.5 = 0.0417 \text{ atm}$$

It can be seen that although the equilibrium has shifted to the left, the equilibrium constant is unchanged.

When pressure is increased the molecules are pushed closer together, so effectively the concentration increases. This generally produces an increase in the rate of a reaction.

Catalyst

The presence of a catalyst increases the rate of a reaction of both forward and backward reactions in proportion. This means that the use of a catalyst does not shift an equilibrium in any particular direction and does not change an equilibrium constant.

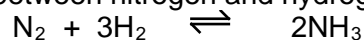
The table below gives a summary of the effect of changing various conditions on equilibrium.

| Change in condition | Reaction | Effect on | |
|----------------------|-------------------------------------|----------------------|----------------------|
| | | Equilibrium position | Equilibrium constant |
| Temperature increase | Exothermic | Shifts to left | Decreases |
| Temperature decrease | Exothermic | Shifts to right | Increases |
| Temperature increase | Endothermic | Shifts to right | Increases |
| Temperature decrease | Endothermic | Shifts to left | Decreases |
| Pressure increase | Molecules on LHS > Molecules on RHS | Shifts to right | No change |
| Pressure decrease | Molecules on LHS > Molecules on RHS | Shifts to left | No change |
| Pressure increase | Molecules on LHS < Molecules on RHS | Shifts to left | No change |
| Pressure decrease | Molecules on LHS < Molecules on RHS | Shifts to right | No change |
| Catalyst added | | No change | No change |

Industrial Processes

Information on entropy change, enthalpy change and equilibrium constants can be used to select conditions for industrial processes.

The reaction between nitrogen and hydrogen to produce ammonia is a reversible reaction.



If nitrogen and hydrogen are mixed and heated virtually no ammonia is produced.

Since the value of ΔS_{TOTAL} is positive it is clear that the reaction is feasible, so the choice of conditions is key to the production of ammonia in this reaction.

- It is an exothermic reaction, so a low temperature favours the formation of ammonia.
- There are two molecules of gas on the right hand side and four on the left, so a high pressure favours the formation of ammonia.

The problem in the production of ammonia is that at the low temperature required for a good equilibrium position, the rate of reaction is so slow as to be non-existent.

A high pressure increases the concentration of the gases, and so increases the rate. The problem with creating a pressure is that it is very expensive in terms of building the plant and in terms of maintenance.

Haber devised conditions whereby ammonia could be produced economically.

TEMPERATURE High temperature favours good rate
 Low temperature favours equilibrium

PRESSURE High pressure favours good rate and good equilibrium
 Low pressure is cheaper

TYPICAL CONDITIONS

| | |
|-------------|---------|
| Pressure | 250 Atm |
| Temperature | 450°C |
| Catalyst | Iron |

Under these conditions ammonia can be produced economically. The use of a catalyst means that a good rate can be produced at a moderate temperature which allows about 10 - 15 % ammonia to be produced.

Although 10% is not a particularly good yield, the unused gases are recycled, so there is no waste, and a rapid reaction means that good quantities of ammonia are produced.

In this process as in other industrial processes, the system never actually attains equilibrium. This is because it is more economical to remove the reaction mixture from the reaction vessel when a certain amount of product has formed, separate out the product and recycle to reactants.

Choice of catalyst is very important for the chemical industry. The iron catalyst for the Haber process becomes more effective when small quantities of other materials called promoters are mixed with the iron.

The table below shows the effect of promoters on the iron catalyst in the Haber process at a temperature of 400°C and a pressure of 200 atm.

| Catalyst | Promoter | % ammonia in exit gases |
|----------|---|-------------------------|
| Iron | None | 3 – 5 |
| Iron | K ₂ O | 8 – 9 |
| Iron | K ₂ O + Al ₂ O ₃ | 13 – 14 |

A more effective catalyst means that lower temperatures can be used to achieve the same rate, with the result that the equilibrium yield can be increased. Alternatively a lower pressure could be used so making the process less expensive and safer.

The chemical industry takes various steps to make reactions more efficient, so saving resources and preventing wastage, thereby making them more sustainable.

For example in the Haber process, with an exothermic reaction, the gases emerging from the reactor are cooled. Incoming gases can be used to do this, which saves energy as these gases do not need to be heated using fossil fuels.

The Haber process has been used as an example of how conditions can be selected to control the reaction and how the process can be made more efficient. These are applicable to the whole chemical industry.

In general the chemical industry chooses conditions for a process which makes that process safe and economically effective.

Another way in which the creation of a product can be made more efficient is to choose an alternative reaction with improved atom economy.