edexcel

INTERNATIONAL GCSE (9-1)

Chemistry (4CH1)

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TOPIC GUIDE:

Chemical equilibria

Pearson Edexcel International GCSE in Chemistry (4CH1) and Science (4SD0 and 4SS0)

Pearson

Strategies for teaching chemical equilibrium

Introduction

In 1984 R.T. Allsop and N.H. George wrote an article, published in Education in Chemistry, entitled 'Le Châtelier – A Redundant Principle?' in which they argued that the use of the principle was counterproductive to the understanding of chemical equilibrium. Despite the compelling arguments put forward in this article, and the evidence from a number of research papers published within the last twenty years showing that reliance on Le Châtelier to explain the qualitative effects of external changes on the position of equilibrium leads to many misconceptions in both students and teachers alike, the principle has remained a prominent a feature of many Chemistry specifications in both England and worldwide. Although Le Châtelier's Principle is not required for teaching the International GCSE Chemistry specification, a number of students refer to it in answers.

One problem with Le Châtelier's Principle is that it fails to predict the outcome of changes to conditions in a number of cases, particularly reactions involving gases where a change in temperature will lead to a change in pressure in a closed system. For example, a test administered to two samples of chemistry teachers in Nanjing, China revealed that, of the 109 teachers who participated in the test, only one understood that adding more CS_2 gas to the equilibrium system $CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$ at constant pressure and temperature can shift the equilibrium to either the reactant or product side, depending upon the amount of CS_2 in the initial equilibrium system. Most of the teachers relied on Le Châtelier's principle and thus made erroneous predictions.

The qualitative effects on the position of equilibrium of changes in concentration of reactant, temperature and pressure are part of the subject criteria for GCE Chemistry, and hence must be included in A level specifications. It is for this reason that the qualitative effects of changes in temperature and pressure have been included in the Edexcel International GCSE Chemistry specification.

So, how can this topic be taught without reference to Le Châtelier's Principle?

Teaching dynamic equilibrium at GCSE level

The answer to the previous question lies in the use of van't Hoff's rules.

An appropriate wording of these rules for use at both GCSE and AS level is:

- an increase in temperature, at constant pressure, will shift the equilibrium in the direction of the endothermic reaction
- a decrease in temperature, at constant pressure, will shift the equilibrium in the direction of the exothermic reaction
- an increase in pressure, at constant temperature, will shift the equilibrium to the side where there are fewer moles of gas
- a decrease in pressure, at constant temperature, will shift the equilibrium to the side where there are more moles of gas

If questions are now asked in which one, **and only one**, variable is changed, then they can be answered by direct application of these simple rules.

It is important to point out that the rules are predictors only; they do not offer any explanation as to why the changes take place. Explanations can only be sought via consideration of the relevant equilibrium constants, and is best dealt with at A level.

Some examples of equilibrium situations

Let's now consider some examples where the rules can be applied.

1. Carbon monoxide and hydrogen are used in the manufacture of methanol.

   The reaction is reversible and can reach a position of equilibrium.

   $$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91 \text{ kJ/mol}$$

   The reaction is carried out at a pressure of about 100 atmospheres and a temperature of 250 °C.

   (a) State the effect on the yield of methanol of carrying out the reaction at a lower temperature, but at the same pressure.

   (b) State the effect on the yield of methanol of carrying out the reaction at a higher pressure, but at the same temperature.

   Answers:

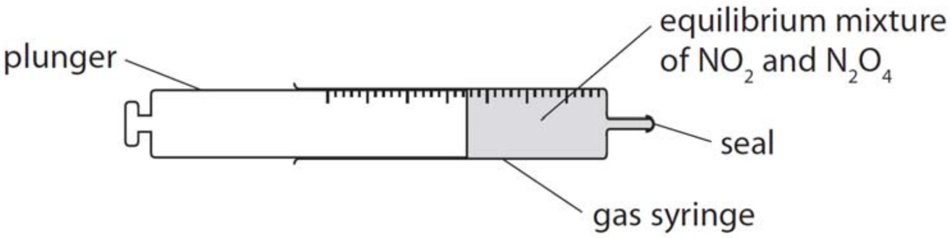
   (a) The yield of methanol would increase. A decrease in temperature shifts the equilibrium in the direction of the exothermic reaction; hence the equilibrium position shifts to the right because the forward reaction is exothermic.

   (b) The yield of methanol would increase. An increase in pressure shifts the equilibrium to the side where there are fewer moles of gas; hence the equilibrium position shifts to the right because there are fewer moles of gas on the right hand side of the equation.

2. Nitrogen dioxide (NO_2) and dinitrogen tetraoxide (N_2O_4) exist together in equilibrium.

   $$\underset{\text{brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{colourless}}{N_2O_4(g)} \qquad \Delta H = -58 \text{ kJ/mol}$$

   A gas syringe contains a sample of an equilibrium mixture of the two gases. The mixture is brown in colour.



   The plunger is pulled out to reduce the pressure of the gaseous equilibrium mixture. The colour of the mixture first of all changes to light brown as it now occupies a larger volume. However, it then goes darker brown in colour as a new equilibrium is established.

   State why mixture changes from light brown to a darker brown. Justify your answer.

   Answer:

   The mixture goes darker because more NO_2 is formed. A decrease in pressure shifts the equilibrium to the side where there are more moles of gas. The equilibrium position shifts to the left hand side as there are more moles of gas on this side.

N.B. The observant amongst you will have spotted a potential flaw in the argument put forward. The pressure is not the only factor to have changed. The volume has changed as well. However, there is another rule that van't Hoff produced that covers this situation. It is: 'An increase in volume, at constant temperature, will shift the equilibrium to the side where there are more moles of gas'.

Hence, the increase in volume produces the same result as the decrease in pressure.

How to demonstrate in the laboratory

- The nitrogen dioxide/dinitrogen tetraoxide mixture can be generated by heating lead(II) nitrate in a boiling tube connected to the gas syringe with rubber tubing.
- Be careful to place a wad of cotton wool in the neck of the boiling tube since lead(II) nitrate decrepitates on heating, and work in a fume cupboard.
- When sufficient gas mixture has been collected, disconnect the rubber tubing and seal the end of the gas syringe with a plastic cap or similar.
- You can now increase or decrease the pressure of the gas in the syringe by pushing or pulling the plunger.
- When pushing the plunger you may have to hold your finger over the plastic cap. Be sure to wear protective gloves if you do this.

Remember, it is your responsibility to carry out a risk assessment, based on local conditions, on this procedure before doing the experiment. If in doubt CLEAPPS can always help.

Use this link to see a video of this experiment:
https://www.youtube.com/watch?v=L6GfhqoCz8Y

3. Iodine monochloride reacts reversibly with chlorine to form iodine trichloride.

$$\underset{\text{dark brown}}{ICl} + Cl_2 \rightleftharpoons \underset{\text{yellow}}{ICl_3}$$

The reaction mixture is allowed to reach equilibrium in a sealed tube. The tube is then heated. The reaction mixture becomes darker brown in colour.

State whether the backward reaction is exothermic or endothermic. Justify your answer.

Answer:

The backward reaction is endothermic. An increase in temperature shifts the equilibrium in the endothermic direction. Since the mixture has become darker brown in colour, more ICl has been formed, so the equilibrium has shifted to the left.

We can now return to the problem set to the teachers in Nanjing.

Remember they were asked to predict the effect that adding more CS_2, at constant temperature and pressure, would have on the following equilibrium:

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

The reason why a qualitative approach cannot solve the problem is that two competing changes are taking place.

On the one hand, more CS_2 is being added, and this change alone would result in a shift in the equilibrium position to the right hand side.

On the other hand, since the change is being made at constant pressure, there must be an increase in volume. This change alone would result in a shift in the equilibrium position to the left hand side.

Qualitative predictions do not tell us which effect is the greater, so it is impossible to state which way the equilibrium will shift.

[For those of you who are interested, the solution is as follows:

$$Q_c = \frac{\left(\frac{nCH_4}{V}\right)\left(\frac{nH_2S}{V}\right)^2}{\left(\frac{nCS_2}{V}\right)\left(\frac{nH_2}{V}\right)^4} = \frac{(nCH_4)(nH_2S)^2V^2}{(nCS_2)(nH_2)^4}$$

If the new $\frac{V^2}{(nCS_2)}$ ratio is greater than the original ratio in the K_c expression, then $Q_c > K_c$ and the equilibrium must shift to the left

If the new $\frac{V^2}{(nCS_2)}$ ratio is less than the original ratio in the K_c expression, then $Q_c < K_c$ and the equilibrium must shift to the right

This is the sort of argument that one would hope a good A-level student would be capable of, particularly if they are planning to read Chemistry at tertiary level.]

Setting questions on dynamic equilibrium

When setting questions on dynamic equilibrium it is very important to phrase the question in such a way that it can be answered. That may seem an obvious statement to make, but questions that at first sight seem possible to answer can, in fact, be impossible to do so.

For example, the following question cannot be answered:

$$\underset{\text{brown}}{2\,NO_2(g)} \rightleftharpoons \underset{\text{colourless}}{N_2O_4(g)} \qquad \Delta H = -58\,\text{kJ/mol}$$

A mixture of $NO_2(g)$ and $N_2O_4(g)$ is placed in a sealed tube and allowed to reach equilibrium at 20 °C . The mixture is light brown in colour.

State what will happen to the colour of the mixture if the sealed tube is placed in water at a temperature of 60 °C and allowed to re-establish equilibrium. Justify your answer.

In all likelihood, a candidate faced with this question will focus on the change in temperature and conclude that the mixture will become darker brown in colour as the equilibrium shifts to the left, since the backward reaction is endothermic.

However, this overlooks the fact that the pressure of the gaseous mixture has also increased, since it is in a sealed container. This increase in pressure, if it occurred alone, would shift the equilibrium to the right, where there are fewer moles of gas.

There are competing effects and qualitative arguments cannot predict which is the greater.

However, if the question is phrased as follows, it can be answered:

A mixture of $NO_2(g)$ and $N_2O_4(g)$ is placed in a sealed tube and allowed to reach equilibrium at 20 °C. The mixture is light brown in colour.

The tube is placed in water at a temperature of 60 °C and the mixture is allowed to re-establish equilibrium. The mixture goes darker brown in colour. State why this happens and justify your answer.

Answer:

The equilibrium has moved to the left to produce more $NO_2(g)$. This happens because the backward reaction is endothermic and an increase in temperature shifts the equilibrium in the direction of the endothermic reaction.

There is no need to consider the increase in pressure in this case because the increase in temperature obviously has the greater effect, since the mixture has gone darker brown in colour.

Videos showing the effect of temperature on this equilibrium can be found at:

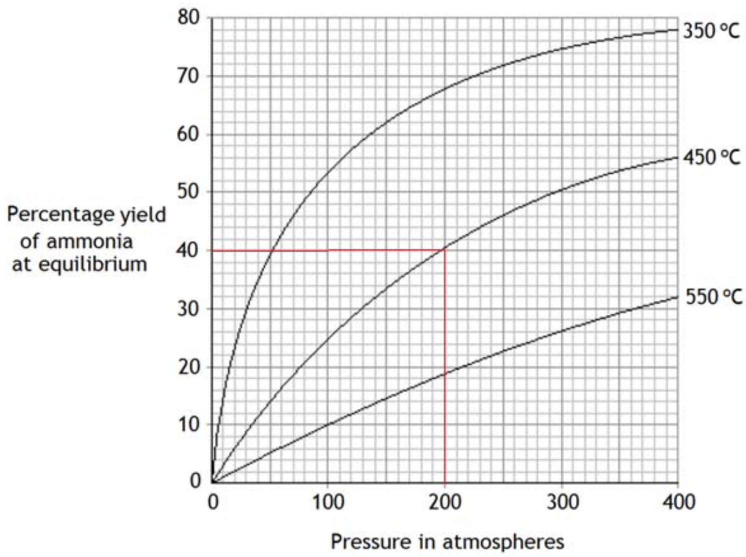
https://www.youtube.com/watch?v=tlGrBcgANSY

https://www.youtube.com/watch?v=uLA_nWvLtJc

Equilibrium and the Haber process

A problem arises here, since the reaction mixture does not reach a position of equilibrium in the reaction chamber, presumably because it is flowing through an open chamber and does not remain for long enough in contact with the iron catalyst.

The graph shows the relationship between the percentage yield of ammonia **at equilibrium** and the temperature and pressure employed.



At a temperature of 450 °C and a pressure of 200 atm, the **equilibrium** yield of ammonia is 40 %.

When these conditions are employed in the industrial process the yield, for each pass of the mixture through the reaction chamber, is only about 15 %. Clearly the mixture does not attain equilibrium in the chamber.

Care, therefore, has to be taken when asking for reasons why specific conditions of temperature and pressure are used in the industrial process. The answer **cannot** be linked to the **equilibrium** yield of ammonia.

Dynamic equilibrium

Two useful links to demonstrate the concept of dynamic equilibrium are:

https://www.youtube.com/watch?v=yFqYrBxbURY

https://www.youtube.com/watch?v=wlD_ImYQAgQ