THE INSTITUTE OF EDUCATION

SUBJECT: CHEMISTRY

LEVEL: HIGHER

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EQUILIBRIUM

In the equations we have come across so far they have all 'gone to completion':

$$A + B \rightarrow C$$

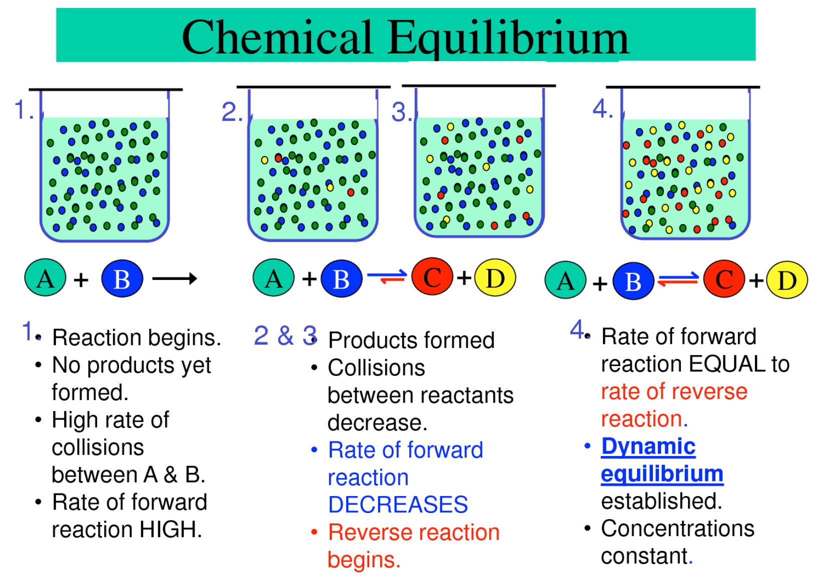
Reactant A has reacted with reactant B to give product C. The reaction is finished once either A or B runs out.

Not all reactions 'go to completion', they are reversible:

$$A + B \rightleftharpoons C + D$$

In the above equation reactant A reacts with reactant B to give product C and D, but C and D react also to give A and B. The reaction **never stops/ceases.**

However we can say that the reaction is considered 'finished' as the amounts of A, B, C and D remain constant as long as the temperature stays constant. We have produced the maximum amount of all substances in the system as possible at that particular temperature.



When we examine a reversible reaction we see the following:

- Initially the reactants are present but there is no product.
- So the rate of the forward reaction begins quickly but decreases with time.
- Initially the rate of the reverse reaction is non-existent but increases over time as more product is formed.
- As time passes the rate of the forward reaction begins to decrease and the rate of the reverse reaction will increase so eventually we will reach a stage when the rate of the forward will equal the rate of the reverse reaction. When this happens the reaction is said to have reached a state of equilibrium.

> CHEMICAL EQUILIBRIUM
> **Defn – a system is said to have reached a state of equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.**

The reaction has not stopped hence it is in a state of dynamic equilibrium. However once a reaction has reached equilibrium it has gone as far as it can go, so the reaction is considered 'finished'.

The amounts of reactants and products remain constant at the temperature that the reaction was carried out.

DYNAMIC EQUILIBRIUM

Defn - Both the forward and reverse reactions occur at the same time.

LE CHATELIER'S PRINCIPLE

Defn – when a system at equilibrium is subjected to a stress such as a change in temperature, pressure or concentration the system will alter to oppose the effect of the stress.

Concentration

If a substance is removed (decrease in concentration) the reaction that will be favoured will be the one that makes that substance.

If a substance is added (increase in concentration) the reaction that will be favoured will be the one that uses up that substance.

Example –

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Question -

State and explain the effect on the position of equilibrium when (a) more NH_3 is added, (b) some N_2 is removed.

Answer –

(a) The position of equilibrium will move to the LEFT favouring the REVERSE reaction so as to use up the extra NH_3 that was added.

(b) The position of equilibrium will move to the LEFT favouring the REVERSE reaction so as to make more N_2.

Temperature

If the temperature is **decreased**, the **EXOTHERMIC REACTION** will be favoured. This is because exothermic reactions give out heat and this heat will replace the heat that was removed.

If the temperature is increased, the ENDOTHERMIC REACTION will be favoured. This is because endothermic reactions take in heat and this will remove the extra heat that was given to the system.

Example –

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -92 \text{ kJ/mol}$$

Note- we can see from this equation that the forward reaction is an exothermic one as ΔH is negative. Therefore the reverse reaction will be endothermic.

Question -
State and explain the effect on the position of equilibrium if (a) the temperature is increased, (b) the temperature is decreased.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -92\text{kJ/mol}$$

Answer –
(a) The position of equilibrium will move to the LEFT favouring the REVERSE reaction as it is endothermic and will use up the extra heat that was added.
(b) The position of equilibrium will move to the RIGHT favouring the FORWARD reaction, as it is exothermic and will replace the heat that was removed.

Note 1– every equation has to be examined individually to see which are the endothermic and exothermic reactions. Then decide whether forward or reverse reaction is favoured.

Note 2 – if the heat change for the reaction is 0, then a change in temperature will not change the position of equilibrium.

Pressure (for gaseous systems only)
If the pressure is **INCREASED** the system will favour the side with the **LEAST** number of moles (as this will bring the pressure back down).

If the pressure is DECREASED the system will favour the side with the MOST number of moles (as this will bring the pressure back up).
Example:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Note - As we can see from this equation there are 4 moles of substance on the LEFT of the equation and there are only 2 moles of substance on the RIGHT.

Question –
State and explain the effect on the position of equilibrium on the above system when (a) the pressure is increased and (b) the pressure is decreased.

Answer –
(a) The position of equilibrium will move to the RIGHT favouring the FORWARD reaction as the forward reaction produces less moles which will bring the pressure down again.

(b) The position of equilibrium will move to the LEFT favouring the REVERSE reaction as the reverse reaction produces more moles, which will bring the pressure up again.

What happens when there are equal numbers of moles on both sides of the equation?

Example –

$$H_2 + I_2 \rightleftharpoons 2HI$$

In this equation there are 2 moles of substance on both sides of the equation hence increasing or decreasing the pressure will have no effect on the position of equilibrium.

TRICK QUESTION – REMEMBER THAT CHANGES IN PRESSURE NEVER HAVE AN EFFECT ON SYSTEMS THAT ARE NOT GASEOUS….THIS HAS TRICKED MANY STUDENTS IN THE PAST!!!

SAMPLE QUESTIONS

1. Hydrogen gas can be manufactured according to the following reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H = 205 kJ/mol$$

Describe and explain the effect on the yield of hydrogen for each of the following
(a) Carbon monoxide is removed.
(b) The pressure is increased.
(c) The temperature is decreased.
(d) A catalyst is added.

Note – this reaction is known as 'steam reforming of natural gas'. Used to produce hydrogen for the Haber process for the manufacture of ammonia. YOU NEED TO KNOW THIS!

2. When concentrated hydrochloric acid is added to bismuth (III) chloride a colourless solution of $BiCl_4^-$ ions is formed. As water is slowly added to this solution a white ppt of bismuth (III) chloride oxide ($BiOCl$) appears and the following dynamic equilibrium is established:

$$BiCl_4^- + H_2O \rightleftharpoons BiOCl + 2HCl + Cl^-$$

(a) Explain the underlined word.
(b) State and explain what you would observe as concentrated hydrochloric acid is added to the above equilibrium system.
(c) If, having added the concentrated hydrochloric acid as described in (b) above, sufficient water were added, what change, if any, would you notice in the equilibrium system? Explain your answer.
(d) Name and state in full the principle on which your explanations are based. **(LCH 1989).**

Kc –THE EQUILIBRIUM CONSTANT in terms of molar (mol/l) concentrations

It has been found that at a given temperature there is a mathematical relationship between the concentrations of the reactants and the concentration of the products in an equilibrium mixture.

For example, consider the following reaction:

$$aA + bB \rightleftharpoons cC + dD$$

By experiment it has been found that the concentrations of all species at equilibrium can be related by

$$Kc = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where Kc = the equilibrium constant expression in terms of molar concentrations.

$[A]^a$ = the concentration of the substance in **moles per litre to the power of the number of moles in the balanced equation**.

Note – the RHS are on top and the LHS are on the bottom of the expression.
Examples –

Write the equilibrium constant expression, Kc for the following reactions:

1.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Answer -

$$Kc = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

2. $CH_4 + H_2O \rightleftharpoons CO + 3H_2$

Answer -

$$Kc = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

Try the following:

1. $H_2 + I_2 \rightleftharpoons 2HI$
2. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

In questions, we will be (a) given or (b) have to work out values for each species in an equation. We will fill these values into the expression for Kc
If we examine the expression Kc we should be able to notice the following:
(a) It is a fraction.
(b) The number on top will refer to the concentrations of the (RHS) .
(c) The number on the bottom will refer to the concentrations of the (LHS).

As it is a fraction there will be two types of fraction it may be:

1. **A top heavy fraction** – this means that Kc will be greater than 1, hence we can see that there was more RHS than LHS present at equilibrium.

2. **A bottom heavy fraction** – this means that Kc will be less than 1, hence we can see that there was more LHS than RHS present at equilibrium.

It is vital that we note that the value of Kc is temperature dependent. If the temperature changes then the value of Kc will change too. REMEMBER THAT THE ONLY FACTOR THAT WILL CAUSE A CHANGE IN THE VALUE OF Kc IS A CHANGE IN TEMPERATURE.

CALCULATIONS INVOLVING Kc

The simplest calculation is when we are given the amounts of each substance at equilibrium – just change to moles per litre and substitute the values in to the expression to get your answer. (has not happened in recent years.)

Otherwise there are two types of calculation involving Kc.

Type 1 – we are asked to calculate Kc.

In this type of calculation, we will be given the grams or moles (or volume) of the reactants at the start and the grams or moles of one of the substances in the equation at equilibrium.

Type 2 – we will be given Kc.

In this type of calculation, we will also be given the grams or moles (or volume) of the reactants at the start but no information about any substance at equilibrium.

Example - Type 1

A mixture of 1.5 moles of hydrogen and 1.5 moles of iodine was allowed to come to equilibrium in a closed vessel at 773K. It was found that 0.35 moles of iodine were present in the equilibrium mixture.

$$H_2 + I_2 \rightleftharpoons 2HI$$

Find the numbers of moles of hydrogen and hydrogen iodide in the equilibrium mixture, and **calculate** the value of the equilibrium constant **(Kc)** at this temperature.

Method for Type 1.

(a) Convert grams to moles if necessary.
(b) If given the volume of the system convert to moles per 1 litre. (If volume is not given it doesn't matter as all units will cancel as there will be equal numbers of moles on both sides of the equation.)
(c) Fill into table the initial moles of reactants and the moles of the substance given in the question at equilibrium. (Remember there will never be any moles of product initially as the reaction has not started yet!).
(d) Work out the change for the substance you have most information about.
(e) N.B. use the molar ratio in the balanced equation to work out the change in the rest of the substances in the question N.B.
(f) Substitute the values at equilibrium into the equilibrium constant expression to calculate Kc at the given temperature.

Answer -

	H_2	I_2	$2HI$
Initial	**1.5**	**1.5**	**0**
Change (molar ratio)	-1.15	-1.15	+2.3
At equilibrium	0.35	**0.35**	2.3

Note – information in bold was given in the question. All other values were calculated. There was no volume given in the question so no need to adjust. We used the molar ratio 1:1:2 in order to work out the changes.

$$Kc = \frac{[HI]^2}{[H_2][I_2]}$$

$$Kc = \frac{[2.3]^2}{[0.35][0.35]}$$

$$Kc = \frac{[5.29]}{[0.1225]}$$

$Kc = 43.18$ @ 773K
(No units as there were equal numbers of moles on both sides of the equation)

Example - Type 2

When a similar experiment, using the same quantities of hydrogen and iodine, was carried out at 623K, it was found that the value of **Kc** had increased to **64**. Calculate (a) the number of moles, (b) the mass, of iodine present in the equilibrium mixture at this temperature.

Method for Type 2

(a) Convert grams to moles if necessary.
(b) If given the volume change to moles per litre, if not given do not do anything.
(c) Fill into the table the initial moles of reactants and remember there will be no product initially.
(d) Use the molar ratio from the balanced equation and x for the change.
(e) Combine together to get moles at equilibrium (these values will be expressed with x).
(f) Substitute these final values into the equilibrium constant expression, Kc, using the value given in the question for Kc.
(g) Work down to a quadratic equation i.e. $ax^2 + bx + c = 0$ and solve for x using the formula $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$.
(h) You will get two answers for x, one will be inappropriate (bigger than the values used initially), ignore this value and use the other value for x to answer the questions involved.

Answer –

	H_2	I_2	$2HI$
Initial	**1.5**	**1.5**	**0**
Change	- x	- x	+ $2x$
At equilibrium	$1.5 - x$	$1.5 - x$	$2x$

Note – information in bold was given in the question. All other values were calculated. There was no volume given in the question so no need to adjust. We used the molar ratio 1:1:2 in order to work out the changes.

Kc = 64 @ 623K

$$\frac{64}{1} = \frac{[2x]^2}{[1.5-x][1.5-x]}$$

$$4x^2 = 64\left(2.25 - 3x + x^2\right)$$
$$4x^2 = 144 - 192x + 64x^2$$
$$4x^2 - 64x^2 + 192x - 144 = 0$$
$$-60x^2 + 192x - 144 = 0$$

$$x = \frac{-192 \pm \sqrt{\left(-192\right)^2 - 4\left(-60\right)\left(-144\right)}}{2\left(-60\right)}$$
$$x = \frac{-192 \pm \sqrt{36864 - 34560}}{-120}$$
$$x = \frac{-192 \pm 48}{-120}$$

$x = \dfrac{-192+48}{-120}$ $\qquad$ $x = \dfrac{-192-48}{-120}$

$x = 1.2$ $\qquad$ $x = 2$ (too large)

(a) Moles of iodine = 1.5 – 1.2 = 0.3 moles

(b) No. of moles X Mr (I_2) = grams

Grams of iodine = $0.3 \times 254 = 7.62$ grams of iodine

ALTERNATIVE FORMS OF EQUATIONS AND THEIR EFFECT ON Kc.

If an equation is written in the following form:

$$H_2 + I_2 \rightleftharpoons 2HI$$

and Kc=43, then Kc for the reaction will be

$$Kc = \frac{[HI]^2}{[H_2][I_2]} = 43$$

However if we halve the equation:

$$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$$

and Kc = 43, then Kc for the reaction will be

$$Kc = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}} = \sqrt{43}$$

Note- when the equation is halved then the new value for Kc = $\sqrt{oldKc}$

If the equation is rewritten in reverse i.e. the reverse of the original equation given in the question.

$$2HI \rightleftharpoons H_2 + I_2$$

and Kc = 43, then Kc for the reaction will be

$$Kc = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{43}$$

Note – when the equation is written in reverse then the new value for

Kc = $\frac{1}{oldKc}$

If an equation is doubled then - Kc= (old Kc) ^{2}

CHEMICAL EQUILIBRIUM – Le Chatelier's principle, the equilibrium constant, Haber process, the Contact process. **© Tara Lyons 2020**

QUESTIONS FROM PAST PAPERS

1. A mass of 16.68 g of phosphorus (V) chloride was heated in a sealed 5 litre vessel at 600K. When equilibrium had been reached at that temperature, the mass of phosphorus (III) chloride was found to be 8.25 g. The equation for the reaction is

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \Delta H = -$$

(i) Write the equilibrium constant (Kc) expression for the reaction and calculate the value of Kc at 600 K.
(ii) Would the values of the equilibrium constant, Kc, have been greater, less or unchanged if the reaction were carried out at 700 K? Explain your answer. (LCH 2001)

2. State Le Chatelier's Principle.
A mixture of 6 moles of methane gas and 6 moles of steam was allowed to come to equilibrium in a closed 60 litre vessel. At equilibrium 50% of the methane had reacted and the temperature in the vessel was 800 C. The equation for the reaction is:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H = 205\text{kJ/mol}$$

(j) Write the equilibrium constant expression (Kc) for the reaction and calculate the value of Kc at 800 C.
(ii) How would the yield of hydrogen be affected (a) if the reaction was carried out at lower temperature, (b) if the reaction were carried out at a lower pressure? Give a reason for your answer in each case.
(iii) The above reaction is used to produce hydrogen for a number of important industrial processes. Name one of these processes. (LCH 1991)

3. Write equilibrium constant expressions in terms of molar concentrations for each of the following reactions and answer the questions that follow.

(a) $CO_2 + H_2 \rightleftharpoons CO + H_2O$
(b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(c) $2BrCl \rightleftharpoons Br_2 + Cl_2$

(i) For which of the three reactions is it necessary to know the volume of the reaction mixture at equilibrium in order to calculate the value of Kc? Explain your answer.
(ii) If the third equation were halved write down the new equation. What effect, if any, will there be on the value of Kc? (LCH 1995)

EXPERIMENT- TO INVESTIGATE LE CHATELIER'S PRINCIPLE.

To demonstrate the effect of concentration changes and temperature changes on the following equilibrium system.

$Fe^{3+} + CNS^- \rightleftharpoons Fe(CNS)^{2+}$
yellow **red**

Apparatus – boiling tubes
Materials – iron (III) chloride, potassium thiocyanate, hydrochloric acid.

Method –

1. A solution of iron (III) chloride and potassium thiocyanate were mixed together in a boiling tube. The colour of the solution was red.
   $$FeCl_3 + CNS^- \rightleftharpoons Fe(CNS)^{2+} + 3Cl^-$$
   yellow **red**
2. Some hydrochloric acid was added. A yellow colour was observed. The position of equilibrium moved to the left, favouring the reverse reaction to use up the extra Cl^- added.
3. Some iron (III) chloride solution was added. A red colour was observed. The position of equilibrium moved to the right, favouring the forward reaction so as to use up the extra iron (III) chloride that was added.
4. Place this red solution in a beaker of boiling water and observe the colour intensity decreasing as the reverse reaction is favoured. Increase in temperature favours the endothermic reaction so the reverse reaction is endothermic.

INDUSTRIAL APPLICATIONS OF LE CHATELIER'S PRINCIPLE.

THE HABER PROCESS FOR THE MANUFACTURE OF AMMONIA.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -93 \text{ kJ/mol}$$

1. The **nitrogen** used is obtained from the **air**. The air is liquefied and then fractionally distilled.
2. The **hydrogen** is obtained from a process called **steam reforming of natural gas**, which is mainly methane.
3. The **catalyst** used is **finely divided iron**, with **aluminium oxide as a promoter**. This means that equilibrium is reached faster and a lower temperature can be used.
4. The ideal temperature for this process is a low temperature as the reaction is exothermic and a low temperature will favour the exothermic reaction. Problem – a low temperature means a slow reaction so a compromise had to be reached. The **temperature** used is about **500 C.**
5. The ideal pressure for this process is a high pressure as there are only 2 moles on the right of the reaction and a high pressure will favour the side with the least number of moles. Problem – a high pressure plant is costly to build and maintain so a compromise had to be reached. The **pressure** used is **200 atm**.

Note – ammonia is used to make fertilisers, cleaning agents, explosives and nitric acid. It is manufactured in Ireland at the IFI plant in Cobh, Co. Cork.

THE CONTACT PROCESS FOR THE MANUFACTURE OF SULFURIC ACID.

There are **3 stages** involved. **The second stage is a reversible reaction**.

Stage 1 – Sulfur is burned in oxygen to produce sulfur dioxide.

$$S + O_2 \rightarrow SO_2$$

Stage 2 – Sulfur dioxide is reacted with oxygen over a catalyst. These must be in close contact with each other, hence the name for the process.

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 \qquad \Delta H = -$$

1. The **catalyst** used is **vanadium pentoxide**, V_2O_5. Platinum is a better catalyst for this reaction but is not used as it is easily poisoned by impurities such as arsenic in the reactants.
2. High pressures will favour the forward reaction as there are less moles, but again high pressure are costly so a **pressure just above atmospheric pressure (4-7 atms)** is used. High pressures can also cause the sulfur dioxide to liquefy.
3. The forward reaction is exothermic so a low temperature is the ideal temperature for the reaction. Again low temperature means slow reaction, so the compromise **temperature of 450 C** is used.

Stage 3 – Sulfur trioxide is reacted with water to make sulfuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Problems arise here. If the sulfur trioxide is reacted with water directly a mist of sulfuric acid that **will not condense** forms over the water. This mist is dangerous. Instead, sulfur trioxide is put in some sulfuric acid that was already made and water is added to this to react with the sulfur trioxide. It is important that 1 mole of water is added for every 1 mole of sulfur trioxide (see balanced equation). Too little water and not all the sulfur trioxide will have reacted, too much water and the sulfuric acid is diluted.

Note – sulfuric acid is used in car batteries, detergents, and paints. World consumption is about 160 million tonnes per year.

QUESTIONS

1. What are the ideal conditions of temperature and pressure for the following industrial processes?

(a) $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ $\triangle$H = 205 kJ/mol

(b) $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$ $\triangle$H= -905 kJ/mol

LEAVING CERT 2019

(*b*) Consider the equilibrium represented by the following balanced equation.

2BrCl (*g*) ⇌ **Br2** (*g*) **+ Cl2** (*g*)

yellow red-brown green

(*i*) Write the equilibrium constant (***K*C**) expression for this reaction. (6)

(*ii*) Calculate the percentage decomposition into bromine and chlorine of 0.200 moles of **BrCl**, placed initially in a 5 litre closed container, and allowed to reach equilibrium at 1200 C according to the equation above. Take the value of ***K*C** at this temperature as 0.220. Give your answer correct to the nearest whole number. (12)

(*iii*) Increasing the pressure on this equilibrium mixture at 1200 C, intensifies the colour of the mixture but does not change the percentage dissociation of **BrCl**. Explain. (7)

LEAVING CERT 2018

Phosgene (**$COCl_2$**) is a toxic gas that was used as a chemical weapon in World War 1. It is now used in chemical synthesis. It is formed from carbon monoxide and chlorine using a charcoal catalyst in a reversible reaction given by:

CO (g) + **Cl_2** (g) $\rightleftharpoons$ **$COCl_2$** (g) $\Delta H = -109.6$ **kJ** $\mathbf{mol^{-1}}$

colourless **green** **colourless**

(*a*) What is meant by a *chemical equilibrium*? (5)

(*b*) Write the equilibrium constant (K_c) expression for the reaction. (6)

(*c*) Under certain conditions in a closed container this equilibrium mixture is green.

State and explain the effect, if any,

(*i*) on the colour of the equilibrium mixture if the pressure is increased by reducing the container size,

(*ii*) on the equilibrium yield of phosgene of using a higher temperature,

(*iii*) on the value of the equilibrium constant (K_c) of using the charcoal catalyst. (18)

(*d*) A 12.0 litre container was filled with 0.200 moles of chlorine and 0.200 moles of carbon monoxide and heated to a certain temperature, *T*. Calculate the value of the equilibrium constant for the reaction at this temperature if 85.0% of the chlorine gas had reacted when equilibrium was reached. (15)

(*e*) Le Châtelier's principle predicts best yields in a certain equilibrium process at low temperatures and high pressures. Suggest reasons why these conditions might *not* be used industrially. (6)

LEAVING CERT 2017

(a) What is meant by a chemical equilibrium? Why is it described as a dynamic state? State Le Châtelier's principle. (14)

Consider the following chemical equilibrium established between dinitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) at a certain temperature T.

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$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

colourless dark brown

(b) Write the equilibrium constant (K_c) expression for the reaction. (6)

(c) The value of K_c for the reaction at T is 0.2. One mole of pure dinitrogen tetroxide was sealed into a container of fixed 10 litre capacity. Calculate the equilibrium concentration, in moles per litre, of each of the gases at temperature T. (18)

(d) The colour of the equilibrium mixture is paler at 0 °C than at T, where T > 0 °C. Explaining your reasoning, deduce whether the decomposition of dinitrogen tetroxide into nitrogen dioxide is an exothermic or an endothermic reaction. (6)

(e) Would there be a change in the value of K_c at T if a different initial concentration of dinitrogen tetroxide were used? Explain your answer. (6)

LEAVING CERT 2016

In the Contact process for the manufacture of sulfuric acid, the key stage is the reaction of sulfur dioxide and oxygen, in contact with a vanadium(V) oxide (**V_2O_5**) catalyst, to form sulfur trioxide. Chemical equilibrium is established according to the following balanced equation.

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g) \quad \Delta H = -196\text{kJ}$$

(*a*) State Le Châtelier's principle. Use Le Châtelier's principle to predict and explain the conditions (i.e. high or low) of (*i*) *temperature*, (*ii*) *pressure,* that would maximise the yield of sulfur trioxide. Explain why the temperature conditions predicted are *not* used industrially. (20)

(*b*) State and explain the effect, if any, of the presence of the catalyst on the equilibrium yield of sulfur trioxide. (6)

(*c*) A mixture of 96 g of sulfur dioxide and 24 g of oxygen was placed in a 50 litre container and reached equilibrium with sulfur trioxide at a certain temperature according to the balanced equation above. At equilibrium, 112 g of sulfur trioxide were present. Write the equilibrium constant (***K***c) expression for this reaction. Calculate the value of ***K***c under these conditions. (24)

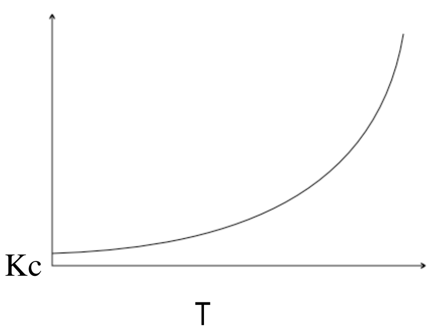
LEAVING CERT 2015

Gas **A** is in equilibrium with gases **B** and **C** according to the following equation.

A(*g*)   **B**(*g*) + **C**(*g*)

The equilibrium constant (K_C) value at 15 C for the dissociation reaction is 4.0. A rigid 10 litre container was filled with 30 moles of gas **A** and stored at 15 C. Calculate the number of gaseous moles at equilibrium in the container. (13)

The graph shows the relationship between temperature (T) and K_C for this equilibrium.



Deduce whether the dissociation of gas **A** is exothermic or endothermic. Explain your reasoning. (6)

Explain how an increase in the storage temperature would affect the pressure of the equilibrium mixture. (6)

LEAVING CERT 2014

Consider the following reversible reaction

$$2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)} \qquad \Delta H = -183 \text{kJ}$$

that has an equilibrium constant (K_c) value of 20.25 at a certain high temperature *T*.

(*a*) Write the equilibrium constant expression for the reaction. (5)

(*b*) Calculate the number of moles of nitrogen gas (N_2) in the reaction mixture at equilibrium when a 2 mole sample of nitrogen monoxide decomposes to nitrogen gas and oxygen gas in a closed container at temperature *T*. (12)

(*c*) State Le *Châtelier' s principle.* (6)

What effect, if any, would an increase in (*i*) the temperature, (*ii*) the pressure, have on the value of K_c for this reaction? Justify your answer in each case. (12)

LEAVING CERT 2013

(a) What is meant by *chemical equilibrium*? Why is a chemical equilibrium described as *dynamic*? (8)

State *Le Châtelier's principle*. (6)

(c) When a yellow solution of iron(III) chloride (**$FeCl_3$**) and a colourless solution of potassium thiocyanate (**KCNS**) were mixed in a test tube, a red colour appeared and the following equilibrium was established:

$$Fe^{3+}_{(aq)} \quad + \quad CNS^{-}_{(aq)} \quad \rightleftharpoons \quad Fe(CNS)^{2+}_{(aq)}$$

yellow red

Explain

(*i*) The effect on the **Fe^{3+}** ion concentration of adding **KCNS** to the equilibrium mixture,

(*ii*) why changing the pressure has no effect on this equilibrium. (9)

(*c*) Write the equilibrium constant (**K_c**) expression for this reaction. (6)

A mixture of 1.0×10^{-3} moles each of iron (III) chloride and potassium thiocyanate was allowed to come to equilibrium in 1 litre of solution at room temperature according to the equation above. It was found that 1.1×10^{-4} moles $\mathbf{Fe(CNS)^{2+}}$ were present in the solution at equilibrium.

Calculate the value of the equilibrium constant ($\boldsymbol{K_c}$) for the reaction. (12)

(d) The red colour faded when the test tube containing the equilibrium mixture was placed in an ice-water bath. State whether the value of $\boldsymbol{K_c}$ for this reaction is bigger or smaller at the lower temperature. Is the forward reaction exothermic *or* endothermic? Justify your answer. (9)

LEAVING CERT 2009

(*a*) Ammonia is formed in the Haber process according to the following balanced equation.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

The table shows the percentages of ammonia present at equilibrium under different conditions of temperature *T* and pressure *P* when hydrogen and nitrogen gases were mixed in a 3:1 molar ratio.

T (K) **Pa(atm)**	**573**	**673**	**773**
10	15	4	1
100	51	25	10
200	63	36	18
1000	92	80	58

(*i*) Find from the table the conditions of temperature and pressure at which the highest yield of ammonia is obtained. (4)

(*ii*) Deduce from the data whether this reaction is exothermic or endothermic. Explain your reasoning. (6)

(*iii*) Identify **one** industrial problem associated with the use of high pressures. (3)

(*iv*) Write an equilibrium constant (***Kc***) expression for this reaction. (6)

(*v*) State the effect on the value of ***Kc*** of using a catalyst. Justify your answer. (6)

LEAVING CERT 2008

A chemical equilibrium is established when eleven moles of hydrogen and eleven moles of iodine are mixed at a temperature of 764K. Initially the colour of the mixture is deep purple due to the high concentration of iodine vapour. The purple colour fades and when equilibrium is established the colour of the mixture is pale pink and there are seventeen moles of hydrogen iodide present.

The equilibrium is represented by the equation

$$\underset{\text{colourless}}{H_{2(g)}} + \underset{\text{purple}}{I_{2(g)}} \rightleftharpoons \underset{\text{colourless}}{2HI_{(g)}} \qquad \Delta H = 51.8 \text{ kJ}$$

(a) What is meant by chemical equilibrium?
When the colour of the mixture has become pale pink, has reaction ceased? Explain. (11)

(b) Write an expression for the equilibrium constant (Kc) for the reaction. (6)
Calculate the value of the equilibrium constant (Kc) at 764K. (12)

(c) State Le Chatelier's principle. (6)
Use Le Chatelier's principle to predict and explain the effect of a decrease in temperature on (i) the yield of hydrogen iodide, (ii) the intensity of colour of the equilibrium mixture. (9)

What change if any, will an increase in the pressure on the equilibrium mixture have on the yield of hydrogen iodide? Explain. (6)

LEAVING CERT 2007

(i) Write the equilibrium constant (Kc) expression for the reaction (7)

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

(ii) Three moles of nitrogen gas and nine moles of hydrogen gas were mixed in a 1 litre vessel at a temperature T. There were two moles of ammonia in the vessel at equilibrium. Calculate the value of Kc for this reaction at this temperature. (12)

(iii) Henri Le Chatelier, studied equilibrium reactions in industry in the late 19^{th} century. According to Le Chatelier's principle, what effect would an increase in pressure have on the yield of ammonia at equilibrium? Explain. (6)

LEAVING CERT 2005

(a) State Le Chatelier's principle. (5)

(b) The value of Kc for the following equilibrium reaction is 4.0 at a temperature of 373K.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(i) Write the equilibrium constant (Kc) for this reaction. (6)

(ii) What mass of ethyl ethanoate would be present in the equilibrium mixture if 15g of ethanoic acid and 11.5g of ethanol were mixed and equilibrium was established at this temperature? (18)

LEAVING CERT 2004

(a) What is meant by chemical equilibrium? Why is it described as a dynamic state? (8)

Consider the following reversible chemical reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -92.4 \text{ kJ/mol}$$

(b) Use Le Chatelier's principle to predict the levels (high or low) of temperature and pressure needed to maximise the yield of ammonia when equilibrium is established. Give a reason (I) for the temperature level you have predicted, (ii) for the level of pressure you have predicted. (12)

(c) Are the temperature levels predicted using Le Chatelier's principle actually used to maximise ammonia yield in industry? Explain your answer. (6)
(d) What is the effect of a catalyst on a reversible reaction? (6)
(e) In an experiment 6.0 moles of nitrogen and 18.0 moles of hydrogen were mixed and allowed to come to equilibrium in a sealed 5.0 litre vessel at a certain temperature. It was found that there were 6.0 moles of ammonia in the equilibrium mixture.
Write the equilibrium constant expression for the reaction and calculate the value of the equilibrium constant (Kc) at this temperature. (18)

LEAVING CERT 2003

State Le Chatelier's principle (7)

A gaseous mixture of hydrogen, iodine and hydrogen iodide form an equilibrium according to the following equation.

$$H_2 + I_2 \rightleftharpoons 2HI$$

(i) Write an expression for the equilibrium constant, K_c, for this system. (6)

(ii) The value of the equilibrium constant, K_c, for this reaction is 50 at 721 K. If 2 moles of hydrogen iodide gas were introduced into a sealed vessel at this temperature calculate the amount of hydrogen iodide gas present when equilibrium is reached. (12)

LEAVING CERT 2002

What colour change will occur if concentrated sulfuric acid is added to the following equilibrium mixture? Give a reason for your answer.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

LEAVING CERT 2002

State Le Chatelier's Principle.
When 30g of ethanoic acid and 23g of ethanol were placed in a conical flask and a few drops of concentrated sulfuric acid added, an equilibrium was set up with the formation of ethylethanoate and water.
The equilibrium is represented by the following equation.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

When the equilibrium mixture was analysed it was found to contain 10g of ethanoic acid.

(i) Write the equilibrium constant expression, K_c, for this reaction. (6)

(ii) Calculate the value of the equilibrium constant, K_c. (12)