**REACTION 1 – NITROGEN DIOXIDE / NITROGEN TETRAOXIDE GAS MIXTURE**

Today your teacher showed you a series of demonstrations for the following gaseous system. All questions below refer to this system.

$$\underset{\text{brown}}{2\ NO_2} \rightleftharpoons \underset{\text{colorless}}{N_2O_4}$$

a) This system is in a gas tube (a sealed container). How would you know the system was at equilibrium?

There is no observable change - constant/unchanging brown colour

Temperature & pressure in tube remains constant.

b) What does it mean to say that the system is at equilibrium?

The rates of the forward & reverse reactions are equal. ∴ Concentration of all species is constant.

c) Write the equilibrium law expression for this equilibrium system.

$$K = \frac{[N_2O_4]}{[NO_2]^2}$$

d) You may notice the colour of the gaseous mixture (when at equilibrium at room temperature) is only very pale brown. What does this observation imply about the value of the equilibrium constant for this system?

low $[NO_2]$ ∴ light/pale brown

This implies lots of $NO_2$ has been converted to $N_2O_4$ ∴ at eqm the $[N_2O_4] > [NO_2]$

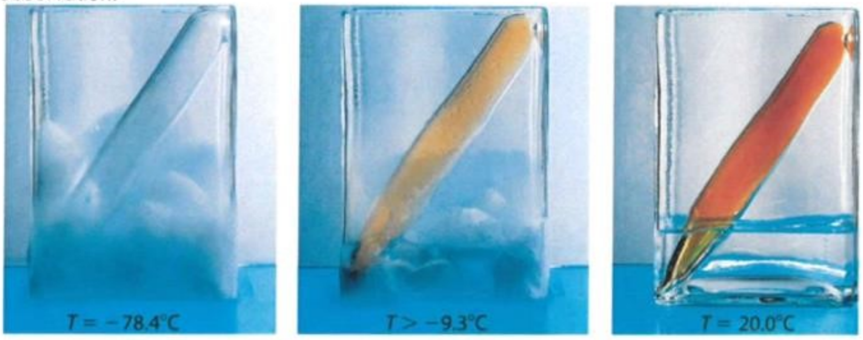
ie: [Products] > [reactants]

∴ K is greater than 1

e) The system below is known to have a negative $\Delta H$. Does this mean the reaction is endothermic or exothermic?

exothermic ($2NO_2 \rightleftharpoons N_2O_4 + heat$)

f) In a demonstration for this $NO_2/N_2O_4$ mixture it was observed that as the temperature of the system is changed the colour of the system at equilibrium also changes. See the image below. (The higher the temperature the darker the equilibrium mixture is). Use Le Chatelier's principle to justify this observation.




$2NO_2 \rightleftharpoons N_2O_4 + heat$

The temperature of the system increases as heat is added

∴ according to le Chat in order to oppose this change the system will favour the reverse endothermic reaction.

because the reverse rxn consumes heat ∴ the temperature of the system comes back down (the change has been opposed)

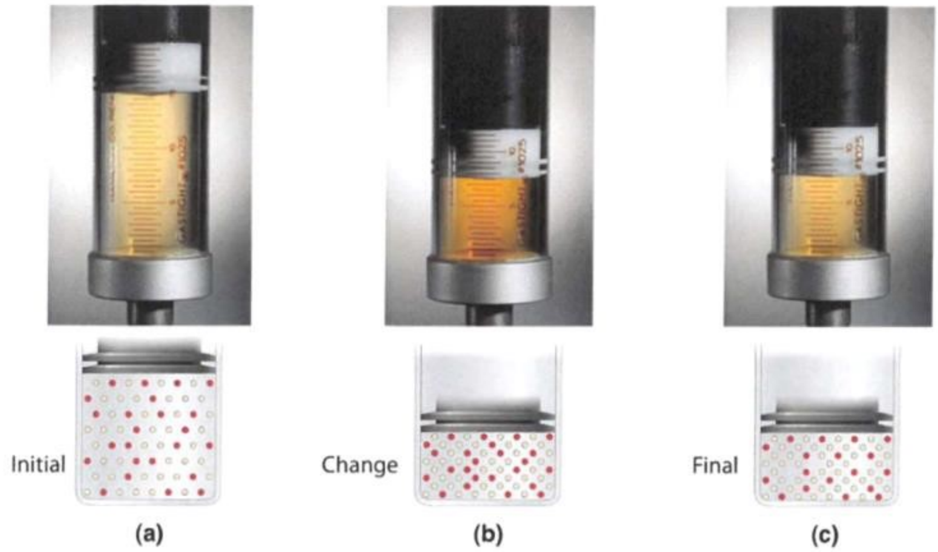
* In favouring the reverse rxn the $[NO_2]$ increases ∴ goes darker brown.

g) Does the value of K increase/decrease/ or not change at all for the three equilibrium systems above?

K decreases as temperature increases.

since $[NO_2]\uparrow$ (reactants), $[N_2O_4]\downarrow$ (products)

In another demonstration the gaseous mixture was compressed. (see image below).




h) Initially the system was at equilibrium and appeared a very pale brown colour (see (a) on the image above). When the container was compressed (volume decreases/overall pressure increases) the colour became instantly darker brown (see (b) on the image above). Can you explain this initial observation.

Simply because upon compression the same amount of $NO_2$ is now in a smaller volume it is more concentrated... so it looks darker brown

i) Then after the initial darkening (due to compression – at time (b) on the image above) it can observed that the colour then fades again to pale brown (see (c) on the image above). Can you show how Le Chatelier's principle can be used to predict this observation?

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

Upon compression the conc of all gases increases ∴ according to Le Chat. the system will favour the forward reaction (because of the 2:1 gas ratio) and thus reduce the moles of gas in the system ie: lower the concentration of gases. Thus opposing the change. Since $NO_2$ is converted to $N_2O_4$ in fwd rxn the brown colour fades as $NO_2$ levels decrease.

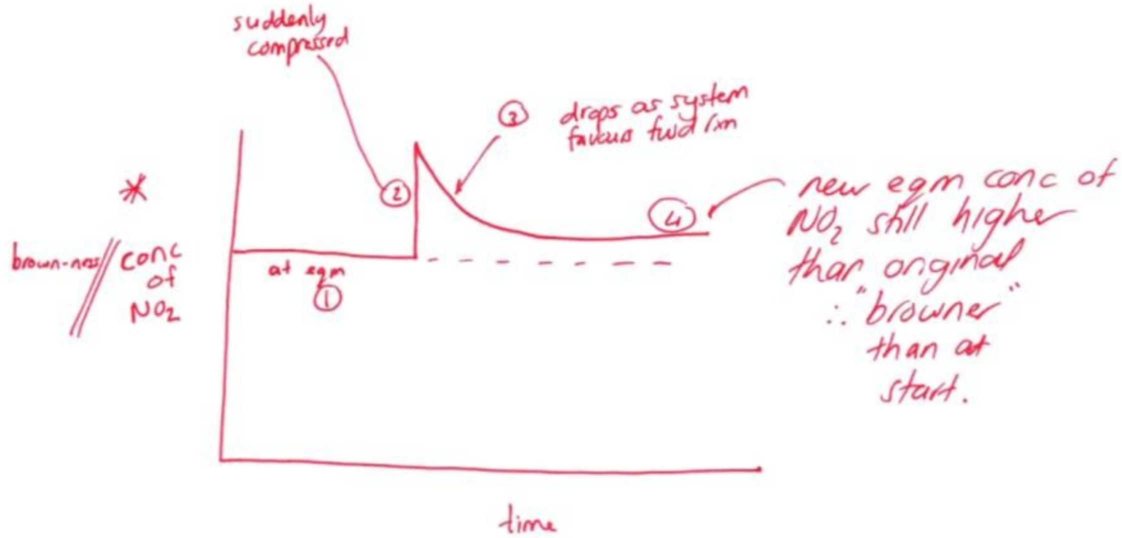
j) Consider the initial equilibrium system at time (a) and the new equilibrium established under higher pressure/lower volume at time (c). The system at time (c) is a little bit darker than the initial equilibrium mixture at time (a). Why?

* The system can only partially oppose the change. Upon compressing (reducing volume) $[NO_2]$ suddenly spikes (hence dark brown) as the system favours the fwd rxn to re-establish eqm the $[NO_2]$ starts going down a bit but not below original levels.

k) Consider the initial equilibrium system at time (a) and the new equilibrium established under higher pressure/lower volume at time (c). Which has the higher K value. (careful!)

K remains constant.
Only changing temperature changes the value of K.

*



**REACTION 2 – THE BLUE BOTTLE**

See below some images from a demonstration involving a mixture of two substances, a colourless molecule that we will refer to as $MB_{red}$ and a blue coloured molecule called $MB_{ox}$ All questions below refer to this system.

$$\underset{\textit{Colorless}}{MB_{red}} + O_2 \leftrightharpoons \underset{\textit{Blue}}{MB_{ox}}$$

In the demonstration the mixture (which initially appeared colourless) is shaken and eventually turns blue.

**A** **B** **C**

a) Justify that at time 'A' the system is at equilibrium.

It is closed and there is no observable change. It remains colourless at time "A"

b) Note the colour of the system at equilibrium at time 'A.' What could you conclude about the position of equilibrium? (is it towards the left or the right?). Justify your answer.

It is colourless

∴ $[MB_{red}]$ is high & $[MB_{ox}]$ is very low

ie: [reactant] " " " [Product] " " "

∴ Position of eqm is towards the left.

K is lessthan 1.

$$MB_{red} + O_2 \rightleftharpoons MB_{ox}$$

c) Upon shaking the bottled the equilibrium shifted and the solution turned blue (see picture on previous page). Can you show how Le Chatelier's principle can be used to predict this observation?

Upon shaking $O_{2(g)}$ dissolves
$\therefore$ $[O_2]_{(aq)}$ increases.

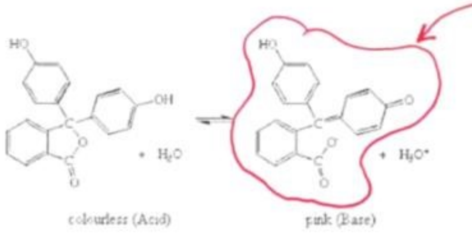
$\therefore$ According to Le Chat the system will favour the fwd rxn as this rxn consumes $O_2$.
$\therefore$ More $MB_{red}$ is converted to $MB_{ox}$
$\therefore [MB_{ox}] \uparrow$ $\therefore$ blue colouring intensifies

d) What is the purpose of using a ⇋ in the equation for this equilibrium system? What does this imply about the reaction(s)?

The reaction is reversible.
It is capable of achieving eqm.
The yield of product is probably not 100%.

**REACTION 3 – ACID BASE INDICATORS**

Consider the following system. A mixture of a weak acid and its conjugate base. The equation below represents this system.



ii. can I call this molecule "P"

a) When sodium hydroxide (base) was added to the system above the colour of the solution changed from colourless to pink.

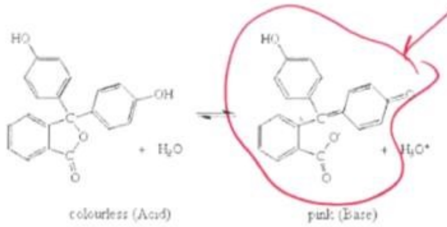
i. Show how Le Chatelier's principle can be used to predict this observation.

NaOH reacted with $H_3O^+$ ∴ $[H_3O^+]\downarrow$ (acid + base)
If $[H_3O^+]\downarrow$ then according to Le Chat. the system will favour the forward rxn to produce more $H_3O^+$ and oppose the change.
In favouring the forward reaction more of the pink coloured product is made & the pink colour intensifies.

ii. Use collision theory to **explain** this observation.

If $[H_3O^+]$ decreases
then the frequency of collisions between "P" and $H_3O^+$ ions decreases
∴ the rate of the reverse reaction decreases such that for a period of time the forward rxn is faster than the reverse.
∴ Rate of formation of "P" is greater than rate of consumption of "P"
∴ [P] increase ∴ pink colour intensifies

b) When sulfuric (acid) was added to the system above the colour of the solution changed back from pink to colourless.




lets call this "P" again

i. Show how Le Chatelier's principle can be used to predict this observation.

$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$

∴ $[H_3O^+] \uparrow$

∴ According to Le Chat the system favours the reverse reaction to consume some of this $H_3O^+$

∴ $[H_3O^+]$ comes back down // the change is opposed. In favouring the reverse rxn the pink molecule is consumed & pink colour fades.

ii. Use collision theory to **explain** this observation.

If $[H_3O^+] \uparrow$

then according to collision theory the frequency of collisions between $H_3O^+$ & "P" increases

∴ Reverse rxn rate increases, such that for a period of time the reverse rxn is faster than the forward

∴ For a period of time "P" is consumed ($\leftarrow$) faster than it is produced ($\rightarrow$)

∴ $[P] \downarrow$ & pink colour fades.

## REACTION 4 – DICHROMATE/CHROMATE MIXTURE

Consider an aqueous solution of yellow potassium chromate ($CrO_4^{2-}$) that contains yellow chromate ions in equilibrium with a very small concentration of orange dichromate ions ($Cr_2O_7^{2-}$). The position of equilibrium is determined by not only the concentrations of each of these ions, but also by the acidity (i.e., the [$H^+$] ions) of the solution.

The equation for this equilibrium is:

$$2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \leftrightharpoons Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$

Recall:

| | |
|---|---|
| $CrO_4^{2-}$ | yellow |
| $Cr_2O_7^{2-}$ | orange |

a) Write the equilibrium law expression for the equilibrium system above.

$$K = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]}$$

b) Given the system above initially appears yellow under the conditions. What does this imply about the magnitude of the equilibrium constant? Explain your answer.

K is small // less than 1

Since [Reactants] is greater than the [Products]

Yellow coloured ion

orange colourd ion

c) When about 2 mL of dilute hydrochloric acid solution was added to about 5 mL of the equilibrium mixture in a test tube. The colour changed from yellow to orange. Use collision theory to explain this observation.

[$H^+$] ↑ when acid is added.

∴ Frequency of collisions between $H^+$ & $CrO_4^{2-}$ inc

∴ Rate of fwd rxn increases

∴ For a period of time (until eqm is re-established) the fwd rxn is proceeding faster than reverse

∴ $Cr_2O_7^{2-}$ is being produced faster than it is being consumed ∴ [$Cr_2O_7^{2-}$] ↑

∴ Orange colour intensifies.

d) The change above result in the establishing of a new equilibrium. Specifically the position of equilibrium shifted right. Did the K value increase in magnitude? Why/Why not?

NO

only a temperature change results in a new K value.

e) When about 2 mL of dilute NaOH solution was added to the now orange equilibrium mixture. The colour changed back to yellow. Use collision theory to explain this observation.

The $OH^-$ in NaOH reacts with the $H^+$ in the system

$\therefore [H^+] \downarrow$

$\therefore$ frequency of collisions between $CrO_4^{2-}$ & $H^+$ decreases

$\therefore$ rate of fwd rxn decreases

$\therefore$ rate of reverse rxn is temporarily faster than the fwd.

$\therefore$ $Cr_2O_7^{2-}$ is converted to $CrO_4^{2-}$ more rapidly than $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$ $\therefore [CrO_4^{2-}]\uparrow$ & $[Cr_2O_7^{2-}]\downarrow$ $\therefore$ yellow colour inc.

f) Consider again the mixture of $CrO_4^{2-}{}_{(aq)}$ and $Cr_2O_7^{2-}{}_{(aq)}$. This time the system is orange initially. The system is then diluted by the addition of a large amount of water. Upon diluting the colour changed from orange to yellow. Show how Le Chatelier's principle can be used to predict this observation. (the equation for the system has been provided again for you)

$$\overset{4}{2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)}} \;:\; \overset{1}{\leftrightharpoons Cr_2O_7^{2-}{}_{(aq)}} + H_2O_{(l)}$$

Upon addition of water the concentration of all aqueous species decreases (diluted)

$\therefore$ according to le chat the system will favour the reverse reaction as it converts 1 (aq) species into 4 (aq) species $\therefore$ increasing the conc of aq species in the system. Thus opposing the change.

Favouring the reverse rxn means lots of $Cr_2O_7^{2-}$ (orange) is converted to $CrO_4^{2-}$ (yellow) $\therefore$ sol$^n$ turns yellow

**REACTION 5 - THICYANATE**

The reaction between $Fe^{3+}$ ions and $SCN^-$ ions is a common equilibrium system used to study Le Chatelier's Principle. The formation of the iron(III) thiocyano complex ion occurs almost instantaneously, the net ionic equation for the equilibrium system being as follows

$$\text{Heat} + Fe^{3+}_{(aq)} + SCN^-_{(aq)} \leftrightharpoons [FeSCN]^{2+}_{(aq)}$$

**(BLOOD RED)**

Initially your teacher added 2 mL of 0.1 $molL^{-1}$ $Fe^{3+}$ ions ($FeCl_{3(aq)}$) to 2 mL of 0.1 $molL^{-1}$ solution of $SCN^-$ ions ($KSCN_{(aq)}$) in a beaker. This was then diluted with distilled water to about 40 mL. The resulting equilibrium is a pale brown colour. Your teacher then numbers 7 test tubes 1 to 7. Add about 5 - 8mLs of the solution made above to the numbered test tubes

By referring to the table below, predict what you will observe when the following steps for each test 1 -7 listed in the table below are carried out. Make sure your answer compares the colour each time with the standard.

| Solution number | Test | Predicted Observations |
|---|---|---|
| 1 | Put aside as the standard | No observable changes here. The solution remains pale brown. |
| 2 | Add 2 mL of $SCN^-_{(aq)}$ solution ($KSCN_{(aq)}$) | Darker blood red |
| 3 | Add solid $FeCl_{3(aq)}$ | $[Fe^{3+}]\uparrow$ ∴ shifts → ∴ darker blood red. |
| 4 | Add 2 mL of $NaF_{(aq)}$ *(Note: adding NaF results in the formation of a compound $FeF^{2+}$)* | $[Fe^{3+}]\downarrow$ ∴ shifts ← Blood red colour fades. |
| 5 | Add 2 mL of $AgNO_{3(aq)}$ *(note this results in the formation of a white ppt AgSCN)* | $[SCN^-]\downarrow$ ∴ shifts ← Blood red colour fades. you will also observe a ppt forming |
| 6 | Warming the solution (increasing the temperature) | system favours fwd endothermic rxn ∴ Darker blood red. |
| 7 | Diluting the mixture | 2 : 1 (aq) species ∴ ← shifts Blood red fades. |

of course it fades ☺

$$Fe^{3+} + SCN^- \rightleftharpoons [FeSCN]^{2+} + \text{heat}$$

a) Explain why heating it caused the equilibrium mixture to change colour?

The reaction above is exothermic.
∴ Upon heating the mixture the rates of both the fwd & reverse rxns increase
But the reverse endothermic reaction increases more than the forward (ie: the reverse rxn is favored)
∴ The $[FeSCN]^{2+}$ ions are used up and the blood colouring decreases/fades.

b) Use collision theory to explain how adding $AgNO_{3(aq)}$ caused the observation you predicted.

1. $[SCN^-]$ ions decreases (due to forming a ppt with $Ag^+$ ions) hence a white AgCl ppt is observed.
2. ∴ frequency of collisions between $Fe^{3+}$ & $SCN^-$ decreases
∴ rate of fwd rxn slows dow
3. ∴ The reverse rxn is temporarily faster than the fwd.
∴ $[FeSCN]^{2+}$ ions are being consumed at a faster rate than they are produced.
4. ∴ $[FeSCN]^{2+}$ conc ↓
∴ Red brown colour fades.

c) Why did the addition of solid $FeCl_3$ impact this equilibrium system? I thought solids did not affect the position of equilibrium.

The $FeCl_3$ is soluble ∴ dissolved ∴ $[Fe^{3+}]$ ↑
∴ the change imposed is that the $[Fe^{3+}]$ conc ↑
∴ according to Le Chat the system will attempt ~~d~~ oppose this change by favouring the fwd rxn
∴ [Fe SN] goes up
& blood-red colour increases

**REACTION 6 - IODINE**

Iodine ($I_2$) is dark coloured solid which sublimes on heating (meaning it bypasses the liquid state) to form a violet coloured gas.

The equation for this equilibrium is:

$$\text{heat} + I_{2(s)} \leftrightharpoons I_{2(g)}$$

Below is a table that compares the colour each time with the standard which is the sealed tube at room temperature.

| Test | Conditions | Observations |
|---|---|---|
| 1 | Room temperature | Pale violet colour observed with a small mass of solid iodine remaining at the bottom of the flask. |
| 2 | Hot temperature (hot water) | Intense violet colour observed with a few grains of solid iodine remaining at the bottom of the flask. |
| 3 | Cold temperature (ice) | Pale colour almost completely disappears. Mass of solid Iodine appears much greater than in the hot temperature system. |

Use Le Chatelier's principle and your understanding of energy changes to justify the observations made in the table above.

The fwd rxn is endothermic
This means upon heating (Test 2) the system will (according to Le Chat.) favour the fwd endothermic reaction to consume heat & oppose the change
∴ $[I_{2(g)}]$ will increase ∴ purple gas colouring intensifies.

Also, removing heat from the system (test tube 3) will cause the system to favour the reverse exothermic reaction.
Thus reducing $[I_{2(g)}]$.
∴ Purple colour fades.

## EXPERIMENT 1

When solid cobalt(II) chloride is dissolved in water, the cobalt(II) ions become 'hydrated'. This means that six water molecules become electrostatically attracted to each cobalt ion. This occurs because the water is polar and the more negative ends of the water molecules are attracted to the positive charge on the cobalt(II) ion. This gives the cobalt(II) ion its characteristically pink colour.

$$CoCl_{2\,(s)} + 6H_2O_{(l)} \rightarrow \underset{\text{(PINK)}}{Co(H_2O)_6^{2+}{}_{(aq)}} + 2Cl^-{}_{(aq)}$$

If the water molecules are removed from the ion and replaced with chloride ions, the colour changes from pink to blue. The equilibrium equation for a system involving hydrated cobalt(II) ions is thus:

$$\underset{\text{(PINK)}}{Co(H_2O)_6^{2+}{}_{(aq)}} + 4Cl^-{}_{(aq)} \leftrightharpoons \underset{\text{(BLUE)}}{CoCl_4^{2-}{}_{(aq)}} + 6H_2O_{(l)}$$

In this series of demonstrations we effectively imposed some changes on the following equilibrium system.

$$\boxed{\underset{\text{(PINK)}}{Co(H_2O)_6^{2+}{}_{(aq)}} + 4Cl^-{}_{(aq)} \leftrightharpoons \underset{\text{(BLUE)}}{CoCl_4^{2-}{}_{(aq)}} + 6H_2O_{(l)}}$$

> CAUTION
>
> Concentrated hydrochloric acid is very corrosive and must be handled with extreme care.

SET UP FOR TEST 1 and TEST 2

Place a pea sized amount of **$CoCl_2.6H_2O_{(s)}$** in a test tube and dissolve in 1-2 mL of deionised water. This step results in the formation of $Co(H_2O)_6^{2+}{}_{(aq)}$

**TEST 1: Add about 5 mL of concentrated hydrochloric acid solution to about 1 mL of cobalt(II) chloride in a test tube.**

Use Le Chateliers principle to **predict** what you may observe.

[Cl⁻] increases
∴ according to Le Chat the system will favour the fwd reaction to consume Cl⁻ & bring [Cl⁻] back down. (opposing the change)
If fwd rxn is favoured then Pink ⟶ Blue colour change will occur.

Now record your observations:

**TEST 2: Add about 2 - 3mL of silver nitrate solution ($AgNO_3$) to the original solution resulting from TEST 1.**

Now record your observations: ______

Use Collision theory to **explain** your observations.

$AgNO_3$ ppt's with $Cl^-$ to form $AgCl$.
$\therefore [Cl^-] \downarrow$
$\therefore$ frequency of collisions between $Cl^-$ & $Co(H_2O)_6^{2+}$ decreases
$\therefore$ rate of fwd rxn decreases
$\therefore$ rate of reverse rxn is temporarily faster than forward.
ie: " " forming $Co(H_2O)_6$ " " " " consuming it
$\therefore$ Blue $\longrightarrow$ Pink colour change will occur.

SET UP FOR TEST 3 and TEST 4

Place about a 2 gram amount of **$CoCl_2.6H_2O_{(s)}$** in a test tube and dissolve in 5 mL of deionised water. This step results in the formation of $Co(H_2O)_6^{2+}{}_{(aq)}$. **Divide this solution between 2 test tubes.**

To BOTH of these test tubes, add dropwise concentrated hydrochloric acid solution until a definite colour change occurs. This establishes the following equilibrium.

$$\underset{\text{(PINK)}}{Co(H_2O)_6^{2+}{}_{(aq)}} + 4Cl^-{}_{(aq)} \leftrightharpoons \underset{\text{(BLUE)}}{CoCl_4^{2-}{}_{(aq)}} + 6H_2O_{(l)}$$

**TEST 3: Heat the first of the test tubes almost to boiling.**

Now record your observations: Upon heating pink → blue colour change occured.

Use Le Chateliers principle to help you decide if the equilibrium system above is exothermic or endothermic.

It must be endothermic
Since heating system has favoured the fwd rxn.
ie: It has favoured the endothermic reaction to oppose the change.

**TEST 4: Dilute the second of the test tubes by slowly adding water.**

Use Le Chateliers principle to **predict** what you may observe.

5:1 (aq) ratio
∴ Upon diluting concentration of all (aq) species decreases
∴ The system favour the reverse rxn to oppose this change
In favouring reverse 1 aq species is converted to 5 (aq) species
∴ concentration of (aq) species goes back up (the change has been opposed)

Now record your observations:

∴ I expect it to turn Pink.