Chem Factsheet

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Equilibrium at AS-Level : Interactively

The idea of "chemical equilibrium" applies to REVERSIBLE reactions in which the forward and backward reactions are both occurring at the same time and are occurring AT EQUAL RATES. This is shown by using the "reversible arrow", $\rightleftharpoons$

The equilibrium between bromine liquid and bromine vapour

Read the following description of a series of observations and then answer the self-assessed questions (SAQ) that follow by crossing out any incorrect options. Check your answers at the end of this FactSheet as you proceed.

THREE stoppered flasks at the same temperature contain different volumes of red bromine liquid. The third flask is TWICE the volume of the other flasks. The orange bromine vapour above the liquid is examined.

OBSERVATIONS	The "orangeness", and hence the concentration, of the bromine vapour is the **same** in all three flasks. Left at constant temperature no visible changes occur.

The following equilibrium exists in this system: $Br_2(l) \rightleftharpoons Br_2(g)$
ie the vapour and liquid co-exist in the system.

Flask 1 is taken to a fume-cupboard, the stopper removed and left for a short time. The cork is then replaced. Note the changes in colour relative to the other flasks.

OBSERVATIONS	The "orangeness" of the vapour is much LESS in this flask than the orange colour in the other flasks. HOWEVER, after leaving the sealed flask for a little while longer, the same "orangeness" is restored.

The temperature of the flasks is then increased by a fixed amount.

OBSERVATIONS	The "orangeness" DARKENS to the same extent in all 3 flasks, even the larger one.

SAQ1 The "same orangeness" in all three flasks indicates that the rate of vaporisation (liquid to vapour) and the rate of condensation (vapour to liquid) are UNEQUAL / EQUAL in all three flasks and that there is constant NUMBER OF MOLES / CONCENTRATION of bromine vapour in each flask.

SAQ2 When the stopper was removed, some bromine LIQUID / VAPOUR escaped and caused the "orangeness" to decrease. After the stopper was replaced, vaporisation of the liquid would be SLOWER / FASTER than condensation of the vapour. Consequently, the "orangeness" of the vapour will DECREASE / INCREASE until the original colour is restored.

SAQ3 The effects of warming show that the balance (equilibrium) between liquid and vapour IS / IS NOT temperature dependent and that the concentration of vapour at equilibrium DECREASES / INCREASES as temperature increases.

SAQ4 The effect observed when the stopper is removed shows that a "steady state" (equilibrium) can only be achieved in AN OPEN / A CLOSED system.

Some further practical exercises to illustrate equilibria

Read the following procedures and corresponding observations, answering all self-assessed questions (SAQ's) as you proceed.

The iodine-hydroxide equilibrium

ie $I_2(aq) + 2OH^-(aq) \rightleftharpoons IO^-(aq) + I^-(aq) + H_2O(l)$

Iodine molecule		Iodate(I) ion	Iodide ion

Place 5 cm³ of 0.1 M iodine solution in a boiling tube. With thorough mixing, add drops of 1.0M sodium hydroxide solution. Continue addition until about 2 cm³ has been added. Note the effect on the colour of the solution.

OBSERVATIONS	The brown colour of the solution gradually fades as more and more drops of alkali are added.

SAQ5 The decrease in the intensity of colour of the solution is caused by the PRODUCTION / CONSUMPTION of iodine molecules as the equilibrium position is caused to move towards the LEFT / RIGHT.
ie as a reactant (OH^-) is added, the equilibrium shifts AWAY FROM / TOWARDS that reactant.

With thorough mixing, add drops of 1.0M nitric acid solution to the solution from the first part of this experiment. Continue addition until about 2 cm³ has been added. Note the effect on the colour of the solution.

OBSERVATIONS	The brown colour of the solution is gradually restored as more and more drops of acid are added.

SAQ6 The increase in the intensity of colour of the solution is caused by the PRODUCTION / CONSUMPTION of iodine as the equilibrium position is caused to move towards the LEFT/RIGHT.

SAQ7 The added nitric acid introduces H^+ ions which react with the OH^- ions in the equilibrium mixture (i.e. $OH^- + H^+ \rightarrow H_2O$). Hence, the observations show that, as an equilibrium reactant (OH^-) is removed (by reaction with $H^+(aq)$), the equilibrium shifts AWAY FROM / TOWARDS that reactant.

Take a fresh 5 cm^3 sample of iodine solution and, with thorough mixing, add drops of 0.1M lead nitrate solution. Continue addition until about 2 cm^3 has been added. Allow the yellow precipitate to settle and note the effect on the colour of the solution.

OBSERVATIONS	The solution becomes a paler brown than the original.

SAQ8 The decrease in the intensity of colour of the solution is caused by the PRODUCTION / CONSUMPTION of iodine as the equilibrium position is caused to move towards the LEFT / RIGHT. ie as a product (I^-) is removed (by reaction with the lead ions to produce insoluble lead iodide), the equilibrium shifts AWAY FROM / TOWARDS that product.

The chromate(VI) - dichromate(VI) equilibrium

ie $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

Yellow chromate(VI) Orange dichromate(VI)

Place 5 cm^3 0.1 M dichromate(VI) solution in a boiling tube. Add drops of 1.0M sodium hydroxide solution until about 2 cm^3 has been added. Note the effect on the colour of the solution.

OBSERVATIONS	The orange solution changes to yellow

SAQ9 The colour change shows the equilibrium has shifted towards the CHROMATE(VI) / DICHROMATE(VI) ions.

SAQ10 The added sodium hydroxide introduces OH^- ions which react with the H^+ ions in the equilibrium ($OH^- + H^+ \rightarrow H_2O$) ie as an equilibrium reactant (H^+) is removed (by reaction with $OH^-(aq)$), the equilibrium shifts WAY FROM / TOWARDS that reactant

Add drops of 0.1M nitric acid to the reaction mixture from the first part until about 2 cm^3 has been added. Note the effect on the colour of the solution.

OBSERVATIONS	The yellow solution changes back to orange.

SAQ11 The colour change shows the equilibrium has shifted towards the CHROMATE(VI) / DICHROMATE(VI) ions. ie as a reactant (H^+) is added, the equilibrium shifts AWAY FROM / TOWARDS that reactant.

NB In general, these observations suggest :

> If a system is at equilibrium, changes in concentration of reagents or products cause the equilibrium position to shift in the direction which OPPOSES the change.
>
> This is known as "LE CHATELIER'S PRINCIPLE"
>
> The same idea applies to ANY change (eg temperature, pressure - see later).

The cobalt(II) - chloride equilibrium

Place 2cm depth of pink aqueous cobalt(II) chloride in a boiling tube.

This contains $[Co(H_2O)_6]^{2+}$ ions.

SAQ 12 What colour are these complex ions? (see above) _______________

Add drops of concentrated hydrochloric acid until there is no further colour change.

OBSERVATIONS	The pink solution changes to blue.

The solution now contains $CoCl_4^{2-}$ ions.

SAQ13 What colour are these complex ions?_______________

The equilibrium concerned here is :

$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$

SAQ14 As chloride ions are added (from the conc HCl), the equilibrium moves towards the LEFT / RIGHT. ie it moves TOWARDS / AWAY FROM the added reactant. ie the tendency is for the added reactant to be PRODUCED / REMOVED.

Take a second sample of aqueous cobalt(II) solution as before and, with thorough mixing, add DROPS of concentrated hydrochloric acid until a purple solution is produced. This contains roughly 50:50 amounts of the two complex ions (pink + blue).

Divide this equilibrium mixture into three equal portions. Leave one at room temperature, cool the second in iced water and warm the third in hot water. Observe any colour changes over the next few minutes.

OBSERVATIONS	At room temperature : Solution remains purple. At lower temperature : Purple solution changes to pink. At higher temperature : Purple solution changes to blue.

SAQ15 As temperature varies, the colour of the mixture VARIES / IS EVENTUALLY CONSTANT. Hence, equilibrium CAN / CANNOT be achieved if temperature varies.

SAQ16 As the temperature is decreased, the equilibrium position moves to produce more of the PINK / BLUE complex. Hence, (see results and equation above) the equilibrium position moves towards the LEFT / RIGHT. Using Le Chatelier, this direction must be the direction which ***opposes*** the applied temperature decrease by ABSORBING / RELEASING heat energy to WARM UP / COOL DOWN the mixture. i.e. it must be an EXOTHERMIC / ENDOTHERMIC reaction in this direction.

SAQ17 As the temperature is increased, the equilibrium position moves to produce more of the PINK / BLUE complex. Hence, (see results and equation above) the equilibrium position moves towards the LEFT / RIGHT. Using Le Chatelier, this direction must be the direction which ***opposes*** the applied temperature increase by ABSORBING / RELEASING heat energy to WARM UP / COOL DOWN the mixture. i.e. it must be an EXOTHERMIC / ENDOTHERMIC reaction in this direction.

The equilibrium between a saturated solution and solute

For a saturated (maximum concentration) aqueous solution of potassium chloride the equilibrium established between solid potassium chloride and dissolved potassium and chloride ions is:

$KCl(s) + (aq) \rightleftharpoons K^+(aq) + Cl^-(aq)$

Suppose some solid radioactive ^{40}KCl *is added.*

After a few minutes the radioactivity level of both solid and solution reach a constant level.

SAQ18 The "added" solid will initially add to the un-dissolved solid (non-radioactive) already present. At this instant, the solid will have LOW / HIGH radioactivity and the solution will have LOW / HIGH radioactivity.

To achieve the observations made, some of the radioactive solid must dissolve and, because the solution is SATURATED, to compensate an equal amount of the dissolved salt must crystallise.

This simultaneous dissolving and crystallising continues until, eventually, the radioactivity is distributed between solid and solution.

SAQ19 This shows that an chemical EQUILIBRIUM STATE is a DYNAMIC / STATIC state. Hence, at a molecular level, at equilibrium the rate of the forward reaction IS / IS NOT equal to the rate of the backward reaction. Hence, "reactants" and "products" CO-EXIST at constant concentrations.

The equilibrium between dinitrogen(iv) tetroxide and nitrogen(iv) dioxide

A gas syringe is filled with dry BROWN nitrogen dioxide and sealed.

At constant temperature, the plunger is then pushed in slowly and observations made. Finally, the plunger is then pulled out slowly and observations made.

OBSERVATIONS	Plunger pushed in : Syringe contents become paler. Plunger pulled out : Syringe contents become darker.

The equilibrium occurring in the syringe is: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

As mentioned, NO_2 is brown. However, N_2O_4 is colourless.

SAQ20 As the plunger is **pushed in**, this causes a momentary DECREASE / INCREASE in pressure inside the syringe. The resulting fading of the brown colour indicates the equilibrium has moved to the LEFT / RIGHT as a result. This side of the equilibrium involves FEWER / MORE gas molecules and hence, corresponds to a LOWER / HIGHER pressure.

SAQ21 As the plunger is **pulled out**, this causes a momentary DECREASE / INCREASE in pressure inside the syringe. The resulting intensification of the brown colour indicates the equilibrium has moved to the LEFT / RIGHT as a result. This side of the equilibrium involves FEWER / MORE gas molecules and hence, corresponds to a LOWER / HIGHER pressure.

SAQ22 In conclusion, when the pressure applied to an equilibrium is **increased** the equilibrium position shifts in the direction which DECREASES / INCREASES the mixture's pressure. It does this by moving towards the side that has FEWER / MORE gas molecules.

When the pressure applied to an equilibrium is **decreased** the equilibrium position shifts in the direction which DECREASES / INCREASES the mixture's pressure. It does this by moving towards the side that has FEWER / MORE gas molecules.

A catalysed reaction

$A(g) + B(g) \rightleftharpoons C(g)$

1 mole of reactant A is mixed with 1 mole of reactant B in each of 2 identical reaction vessels. A small amount of catalyst is added to the second vessel, both vessels are sealed and heated in a thermostatically controlled water bath. At regular time intervals, the concentration of product C in each vessel is measured until it reaches a steady state.

OBSERVATIONS

t (/s)	0	10	20	30	40	50	60
[C]* vessel 1	0	0.10	0.18	0.25	0.30	0.32	0.32
[C]* vessel 2	0	0.20	0.28	0.31	0.32	0.32	0.32

*[C] represents the concentration of C in mol dm^{-3}

SAQ23 These results indicate that a catalyst DOES / DOES NOT influence the position of chemical equilibrium. However, it INCREASES / DECREASES the time required to reach that equilibrium position. Hence, the catalyst must increase the rates of both forward and backward reactions TO DIFFERENT EXTENTS / EQUALLY.

Summary : General characteristics of "equilibrium"

The previous examples suggest the following GENERAL points

1. EQUILIBRIUM IS POSSIBLE ONLY IN A CLOSED SYSTEM. i.e. one in which matter is neither added nor removed.
2. EQUILIBRIUM IS POSSIBLE ONLY AT CONSTANT TEMPERATURE.
3. EQUILIBRIUM CAN BE APPROACHED FROM EITHER DIRECTION.
4. AT EQUILIBRIUM THE INTENSIVE (OR BULK) PROPERTIES (eg concentration, density, colour) OF THE EQUILIBRIUM MIXTURE REMAIN CONSTANT.
5. EQUILIBRIUM POSITION is not affected by a catalyst.
6. CHEMICAL EQUILIBRIUM IS DYNAMIC, NOT STATIC.
7. If a system is AT equilibrium and a CHANGE IN conditions is applied, (eg pressure, temperature, concentrations of reactants or products), then the system will tend to ADJUST to re-establish equilibrium.EQUILIBRIUM IS RE-ESTABLISHED BY THE SYSTEM "SHIFTING" SO AS TO OPPOSE THE CHANGE APPLIED. This is LE CHATELIER'S PRINCIPLE.

Practice Questions

1. Complete the table with respect to the following reaction.

$A(g) + 3B(g) \rightleftharpoons 2C(g)$; $\Delta H = -52$ kJ mole^{-1}

Experimental Change Applied	Resulting Equilibrium Position Shift	Explanation using Le Chatelier's Principle
A added	To LEFT / RIGHT	Addition of A is opposed by: FORMATION / CONSUMPTION of A.
B removed	To LEFT / RIGHT	Removal of B is opposed by: FORMATION / CONSUMPTION of B.
C added	To LEFT / RIGHT	Addition of C is opposed by: FORMATION / CONSUMPTION of C.
C removed	To LEFT / RIGHT	Removal of C is opposed by: FORMATION / CONSUMPTION of C.
Pressure increased	To LEFT / RIGHT	Increase in pressure is opposed by formation of : FEWER / MORE gas molecules to RAISE / LOWER the pressure.
Pressure decreased	To LEFT / RIGHT	Decrease in pressure is opposed by formation of: FEWER / MORE gas molecules to RAISE / LOWER the pressure.
Temperature increased	To LEFT / RIGHT	Increase in temperature is opposed by: a RELEASE / ABSORPTION of energy as the reaction moves in the ENDOTHERMIC / EXOTHERMIC direction.
Temperature decreased	To LEFT / RIGHT	Decrease in temperature is opposed by: a RELEASE / ABSORPTION of energy as the reaction moves in the ENDOTHERMIC / EXOTHERMIC direction.

2. An important reaction in the manufacture of nitric acid is the catalytic oxidation of ammonia.
$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$; $\Delta H = -909$ kJ mol^{-1}
Low pressures and low temperatures would give the maximum equilibrium yield of NO. Explain why. *(4 marks)*

3. Carbon monoxide and hydrogen, along with a copper catalyst, are used in the manufacture of methanol. An equilibrium is established according to the following equation. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$; $\Delta H = -91$ kJ mol^{-1}
   (a) Give **two** features of a reaction at equilibrium. *(2 marks)*
   (b) Explain why an increase in temperature causes a decrease in the equilibrium yield of methanol. *(2 marks)*
   (c) State the effect, if any, of the copper catalyst on the position of this equilibrium at a fixed temperature.*(1 mark)*

4. The following equation represents a reaction in equilibrium. $P(g) + 2Q(g) \rightleftharpoons 2R(g)$
   (a) State and explain the effect on the yield of **R** if the overall pressure is increased. *(3 marks)*
   (b) An increase in temperature causes a decrease in the yield of **R**. State and explain what can be deduced about the enthalpy change for the forward reaction.*(2 marks)*

5. EXTENSION QUESTION
In the previous exercises and questions the following generalisations are deduced by Le Chatelier's Principle for maximising product yield.

	TYPE OF REACTION	BEST FOR INCREASING YIELD
1	The forward reaction is ENDOTHERMIC	HIGH temperature
2	The forward reaction is ENDOTHERMIC	LOW temperature
3	The forward reaction involves an INCREASE in the number of gas molecules	LOW pressure
4	The forward reaction involves an DECREASE in the number of gas molecules	HIGH pressure

Give one reason for:
(a) **NOT** using a **very** high temperature in reaction 1.
(b) **NOT** using a **very** low temperature in reaction 2.
(c) **NOT** using a **very** high pressure in reaction 3.
(d) **NOT** using a **very** low pressure in reaction 4.

Answers To Self-assessed Questions

SAQ1	EQUAL — CONCENTRATION of bromine vapour in each flask.
SAQ2	VAPOUR —. – FASTER — INCREASE — is restored.
SAQ3	IS temperature dependent — INCREASES as temperature increases.
SAQ4	A CLOSED system.
SAQ5	CONSUMPTION of iodine — towards the RIGHT. — AWAY FROM —.
SAQ6	PRODUCTION iodine — towards the LEFT.
SAQ7	TOWARDS that reactant
SAQ8	CONSUMPTION of iodine — towards the RIGHT. – TOWARDS —.
SAQ9	towards the CHROMATE(VI) ions.
SAQ10	AWAY FROM that reactant
SAQ11	DICHROMATE(VI) ions. — TOWARDS that reactant.
SAQ12	PINK
SAQ13	BLUE
SAQ14	RIGHT. — AWAY FROM the added reactant. — REMOVED.
SAQ15	VARIES. — CANNOT be achieved if temperature varies.
SAQ16	PINK complex. — LEFT. — RELEASING — WARM UP — mixture. — EXOTHERMIC reaction in this direction.
SAQ17	BLUE complex. — RIGHT. — ABSORBING – COOL DOWN —mixture. — ENDOTHERMIC reaction in this direction.
SAQ18	HIGH radioactivity — LOW radioactivity.
SAQ19	DYNAMIC state. — IS equal to —.
SAQ20	INCREASE — RIGHT as a result. — FEWER gas molecules —— LOWER pressure.
SAQ21	DECREASE — LEFT as a result. — MORE gas molecules —— HIGHER pressure.
SAQ22	DECREASES the mixture's pressure. — FEWER gas molecules.— INCREASES the mixture's pressure. — MORE gas molecules.
SAQ23	DOES NOT —. — DECREASES the time —. — EQUALLY.

Answers To Practice Questions

1.

Change Applied	Equilibrium Shift	Explanation
A added	To RIGHT	CONSUMPTION of A.
B removed	To LEFT	FORMATION of B.
C added	To LEFT	CONSUMPTION of C.
C removed	To RIGHT	FORMATION of C.
Pressure increased	To RIGHT	FEWER - LOWER
Pressure decreased	To LEFT	MORE - RAISE
Temp. increased	To LEFT	ABSORPTION ENDOTHERMIC.
Temp. decreased	To RIGHT	RELEASE - EXOTHERMIC direction.

2. Low pressure because there are **more molecules on the product side of the equation** and movement in this direction would correspond to an **opposing increase in pressure**.

   Low temperature because the **forward reaction is exothermic** which would result in a release of heat and hence create an **opposing warming up**.

3. (a) **Equal rates** for forward and backward reactions.
   Constant concentrations of reactants and products.

   (b) The equilibrium will **shift in the endothermic direction** when temperature is increased because this **opposes the change by absorbing the added energy** and so creates a cooling down.

   (c) A catalyst has **no effect** on the equilibrium position.

4. (a) Yield will **increase**.
   Because there are **fewer molecules on the product side of the equation** and movement in this direction would correspond to an **opposing decrease in pressure**.

   (b) The reverse reaction must be **endothermic. This direction is favoured when temperature is increased** because this opposes the change by absorbing the added energy and so creates a cooling down. Hence, yield of R is reduced. Hence, the **forward reaction must be exothermic**.

5. **Extension Question**
   (a) Energy costs too high <u>or</u> increased CO_2 emissions during energy generation.

   (b) Rate of reaction too low.

   (c) Energy costs too high during pressure generation <u>or</u> cost of plant to contain pressure too high.

   (d) Rate of reaction too low.

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