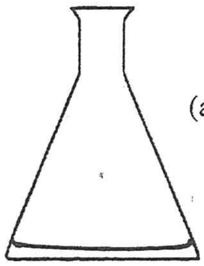
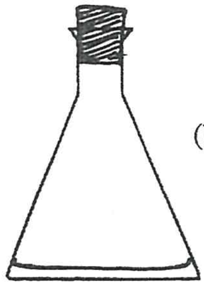
EQUILIBRIUM

Vapour/Liquid Equilibrium.

Q:1 Two flasks (A and B) each have some water added to them but only B is stoppered. They are left undisturbed on a bench for a few days. Describe what you might observe at that time.



(a)



(b)

Observation: ______________________________

____

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Observation: ______________________________

____

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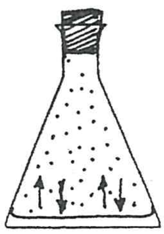
Obviously the water in A has evaporated completely while that in B may has partially evaporated until some kind of equilibrium was established.

> An equilibrium can only occur in a closed system (such as B) and is recognised by the fact that there is no change in macroscopic properties (ie. no change in concentration/pressure/colour, etc.)

We can express the equilibrium that exists in flask (B) as follows.

$$H_2O_{(l)} \quad + \quad \text{heat} \quad \rightleftharpoons \quad H_2O_{(g)}$$



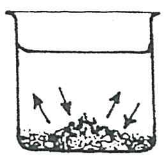
At equilibrium
(i) the rate of evaporation is equal to the rate of condensation.

(ii) The vapour pressure is constant.

Q2: This particular equlibrium is affected by ______________________________?

Solute/Solution Equilibria.

$$C_{12}H_{22}O_{11(s)} \rightleftharpoons C_{12}H_{22}O_{11(aq)}$$



At equilibrium
(i) the rate of dissolving is equal to the rate of crystallisation.

(ii) the mass of excess solute is constant.

3: (a) What other quantity would be constant at equilibrium? ______________________

(b) State two ways by which this equilibrium system could be upset.

(i) By ____

(ii) By ____

hemical Equilibrium

The previous examples were physical systems (ie. no chemical reactions were taking place). A typical chemical system is as follows.

;.1 $$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

Remember, that equilibrium can only exist in a closed system! That is at equilibrium some of all the species involved in the reaction exist. Also at equilibrium, the forward and reverse reaction rates are equal.

quilibrium Constant (K)

For any equilibrium reaction, there is an equilibrium constant (K).

$$K = \frac{\text{concentration of the products (at equilibrium)}}{\text{concentration of the reactants (at equilibrium)}}$$

Note: The value of K for a particular reaction can only be affected by ______________?.

for eg.1. $$K = \frac{[CO][H_2]}{[CO_2][H_2O]} = 0.11 \text{ (at 400° C)}$$

;.2 $$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K = \frac{[HI]^2}{[H_2][I_2]} = 57 \quad \text{(at 425° C)}$$

4: What does a large K indicate about a particular reaction?

____

____

Q5: Write K expressions for the following.
Note that solids and liquids do not form part of a K expression.

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

K = ____________________ (0.21 at 100° C)

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

K = ____________________ (0.11 at 470° C)

(iii) $AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

K = ____________________ (1.7×10^{-10} at 25° C)

(iv) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

K = ____________________ (2.5×10^{-3} at 800° C)

Q6: For the following examples list the predominant species at equilibrium

(i)	$2SO_2 + O_2 \rightleftharpoons 2SO_3$	K =	85
(ii)	$C + H_2O \rightleftharpoons CO_2 + H_2$	K =	100
(iii)	$N_2O_4 \rightleftharpoons 2NO_2$	K =	8.75×10^{-2}
(iv)	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	K =	0.11

Most predominant species is/are

(i) ____________________ (ii) ____________________

(iii) ____________________ (iv) ____________________

Le Chateliers Principle

Chemical systems that are in equilibrium can be easily affected by a change in conditions (e.g. pressure/concentration/tempterature).
Le Chateliers principle helps us predict the direction of the change. It can be stated as follows:

> If a change in conditions is made to a chemical system in equilibrium, then the system will adjust in such a way as to partially counteract the change.

Effect of Changing the Concentration

Suppose the concentration of a reactant is increased:
Le Chateliers principle would suggest that a change will take place to partially counteract this. Hence some of the extra reactant will be consumed in re-establishing equilibrium.

.g.3 $CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

If say CO_2 is added to the system when it is at equilibrium, then the system will adjust so as to favour the forward reaction (right). This will help to partially consume the extra CO_2 added.

)7: Predict the favoured reaction direction in the following cases.

System	Imposed Change	Direction Favoured
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	increase I_2	$\longrightarrow$
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH3_{(g)}$	increase NH_3	
$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$	increase Ag^+	
$MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(g)}$	increase $MgCO_3$	
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	decrease O_2	
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	decrease NO	

Effect of Changing Pressure/Volume.

In equilibrium systems involving gases, changing the volume can alter the pressure and concentration of all the species.

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

If this system is placed under higher pressure (or volume is reduced) the concentration of

both ____________________ and ____________________ will be ____________________.

The system will readjust to the left as this will help to partially reduce the concentration.

.g.5 $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

In this case, changing the volume of the system will affect concentrations equally on both sides. Therefore, there will be no change in equilibrium position (although there will be a change in reaction rate).

Q8: Predict the favoured reaction direction in the following cases.

System	Volume Change	Direction Favoured
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	decrease	
$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$	increase	
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	increase	
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	decrease	
$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$	increase	

Effect of Changing Temperature.

In considering temperature change it is best to include the heat of reaction as part of the equation. In this way heat can be treated as one of the "species" for the purpose of determining change in equilibrium.

e.g.6 For the reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

the heat of reaction (Δ H) is -113 kJ (ie. an exothermic reaction). Find the effect of increasing the temperature! Firstly rewrite the equation so as to include the heat of reaction.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} + 113 \text{ kJ.}$$

An increase in temperature will increase both the forward and reverse reaction rate but the equilibrium will shift to the left (ie. the extra heat can be consumed and satisfy Le Chateliers principle).

Q9: Predict the favoured reaction direction in the following cases.

System	Temperature Change	Direction Favoured
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92$ kJ	decrease	
$H_{2(g)} + I_{2(g)} + 52$ kJ $\rightleftharpoons 2HI_{(g)}$	decrease	
$N_2O_{4(g)} + 57$ kJ $\rightleftharpoons 2NO_{2(g)}$	increase	
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)} + 99$ kJ	increase	
$CaCO_{3(s)} + 179$ kJ $\rightleftharpoons CaO_{(s)} + CO_{2(g)}$	decrease	

ffect of Catalysts.

Catalysts effectively lower the activation energy for a reaction and hence help to increase both the forward and the reverse reaction rates.
Hence they do not effect equilibrium position.

eaction Rates and Equilibrium Position.

These two aspects of any reaction should be treated independently although they may be related. The reaction rate of a reaction may increase but this does not necessarily favour products (as is often imagined).

redicting Changes to a System - Complex Examples.

Some examples are best answered in tabular form.

g.7 The following reaction is at equilibrium.

$$2NO_{(g)} \quad + \quad Br_{2(g)} \rightleftharpoons 2NOBr_{(g)}$$

How would the:
(a) Concentration of all the species
(b) The rates of forward and reverse reactions be affected if
 (i) Some NO is added to the system
 (ii) The concentration of $Br_{2(g)}$ is reduced.
 (iii) The pressure of the whole system is increased.

Imposed Change	[NO]	[Br2]	[NOBr]	$\overrightarrow{\text{R/Rate}}$	$\overleftarrow{\text{R/Rate}}$
Adding NO	Increase				
Reducing [Br_2]					
Increasing Pressure					

*Hint : For each imposed change consider what the final equilibrium position is tending to (from Le Chateliers principle).

Q10: Complete the following table which relates to the reaction shown.

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} + 564\ kJ$$

Imposed	$\overrightarrow{R/Rate}$	$\overleftarrow{R/Rate}$	$[CO_2]$	$[O_2]$
Adding CO				
Increasing Temperature				
Increasing Pressure				
Reducing $[CO_2]$				

Q11: Add suitable headings to the following table to show how reaction rates and concentration of species are affected by increasing pressure, adding a catalyst, and removing $H_{2(g)}$.

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

Industrial Processes - Economic Factors.

In many industrial processes, reaction rates (or more specifically - the rate of attainment of equilibrium) and equilibrium yield are important considerations. The cost of providing desirable reaction conditions has also to be considered and very often a compromise must be made.

eg.8 The HABER process.

Ammonia gas is a very valuable industrial chemical and is produced by the following reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92\ kJ$$

To maximise yield and minimise cost the following is considered.

(i) **Temperature** Low temperature gives the best yield, but this yield is achieved too slowly.

Compromise Temperature 500 C gives an acceptable rate and yield

(ii) **Pressure** - High pressure gives the best yield, however both cost and danger increase with very high pressures.

Compromise Pressure of about 350 Atm is used.

(iii) **Catalyst** An iron/iron oxide catalyst has been found to increase rate of reaction.

We can summarise the factors involved in the HABER process as follows (please complete).

Variable Conditions		R/Rate	% Yield	Conditions Used
Temperature	High Low	fast slow		
Pressure	High Low			
Catalyst	Yes No			

Q:12 One of the reactions involved in the contact process for the manufacture of Sulfuric acid is as follows.

$$2SO_{2(g)} \quad + \quad O_{2(g)} \quad \rightleftharpoons \quad 2SO_{3(g)} \quad + \quad 198\text{ kJ}$$

Complete the table below to indicate the likely conditions that may be used to maximise the economic recovery of $SO_{3(g)}$

Variable Conditions		R/Rate	% Yield	Conditions Used
Temperature	High Low	fast slow		
Pressure	High Low			
Catalyst	Yes No			

TRY THESE.

1. Ethane reacts with oxygen very slowly under normal conditons of temperature and pressure.

$$2C_2H_{6(g)} \quad + \quad 7O_2 \quad \longrightarrow \quad 4CO_{2(g)} \quad + \quad 6H_2O_{(g)}$$

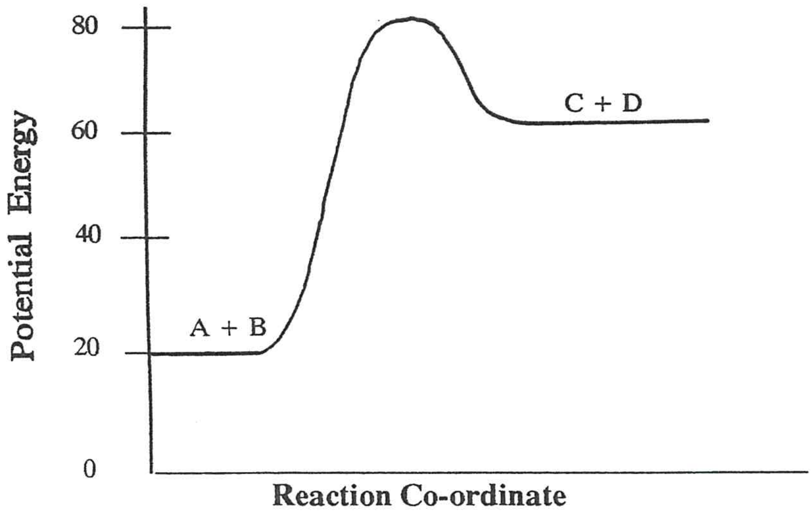
Suggest three ways by which the rate of reaction could be increased.

2. Some Carbon monoxide and Hydrogen gas were placed in a flask and allowed to come to equilibrium as follows:

$$CO_{(g)} + \quad H_{2(g)} \rightleftharpoons HCHO_{(g)}$$

While at equilibrium a very small amount of CO, labelled with radioactive carbon (C^{14}), was added. The amount added was so small as to not significantly alter the CO partial pressure. Several hours later (with the system still in equilibrium) some HCHO was removed and found to be contaminated with C^{14}. Explain clearly how this is possible.

3.



An energy profile diagram is shown above for the reaction

$$A \quad + \quad B \quad \longrightarrow \quad C \quad + \quad D$$

(a) For the forward reaction determine
(i) The activation energy
(ii) The heat of reaction
(iii) What type of reaction it is

(b) For the reverse reaction determine
(i) The activation energy
(ii) The heat of reaction

(c) (i) Draw in a possible catalysed pathway.
(ii) How will this affect heat of reaction?

. Acetic acid, which is a weak acid, ionises as follows.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

At equilibrium less than 1% of the acetic acid molecules have ionised and therefore the concentration of both H^+ and CH_3COO^- ions is very low.
The addition of some NaOH(aq) to the solution increases the concentration of the $CH_3COO^-_{(aq)}$ ions dramatically. Why is this?

. Methanol gas can be broken down to carbon monoxide and hydrogen as follows:

$$CH_3OH_{(g)} \rightleftharpoons CO_{(g)} + 2H_{2(g)} \qquad \Delta H = +90\ kJ$$

Suggest conditions that would enhance this process.

. The following reaction is at equlibrium.

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow 3H_{2(g)} + CO_{(g)} \qquad \Delta H = +206\ kJ$$

Set up a table to show what happens to reaction rate and concentration of each species when:
(i) H_2 gas is partially removed
(ii) The temperature is increased
(iii) The volume is reduced
(iv) A catalyst is added.

7. When CO_2 dissolves in water the following equilibria exist.

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

$$HCO_3^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Small amounts of each of the following substances were added (separately) to see the effect they would have on the apparent solubility of $CO_{2(g)}$ in H_2O.

(a) $NaOH_{(aq)}$ (b) $CH_3COOH_{(aq)}$

(c) $K_2CO_{3(s)}$ (d) $CaCl_{2(aq)}$

Predict the effect in each case and explain.

8. Acetic acid and Ammonium hydroxide are respectively weak acid and base. Their solutions conduct electricity poorly. If the two solutions are combined however, they conduct electricity well! Use equilibrium reactions to explain.

EQUILIBRIUM

Vapour/Liquid Equilibrium.

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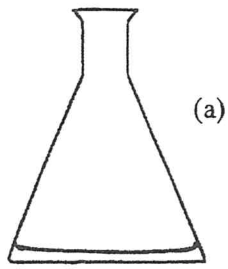
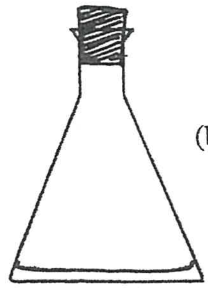


(a)



(b)

Observation: H_2O EVAPORATED & ESCAPED AS FLASK IS NOT SEALED (CLOSED)

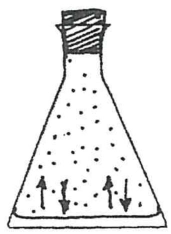
Observation: $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ WATER IN EQUILIBRIUM WITH ITS VAPOUR

Obviously the water in A has evaporated completely while that in B may has partially evaporated until some kind of equilibrium was established.

> An equilibrium can only occur in a closed system (such as B) and is recognised by the fact that there is no change in macroscopic properties (ie. no change in concentration/pressure/colour, etc.)

We can express the equilibrium that exists in flask (B) as follows.

$$H_2O_{(l)} \quad + \quad \text{heat} \quad \rightleftharpoons \quad H_2O_{(g)}$$



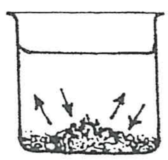
At equilibrium
(i) the rate of evaporation is equal to the rate of condensation.

(ii) The vapour pressure is constant.

Q2: This particular equlibrium is affected by TEMPERATURE?

Solute/Solution Equilibria.

$$C_{12}H_{22}O_{11(s)} \rightleftharpoons C_{12}H_{22}O_{11(aq)}$$



At equilibrium
(i) the rate of dissolving is equal to the rate of crystallisation.

(ii) the mass of excess solute is constant.

3: (a) What other quantity would be constant at equilibrium? $[C_{12}H_{22}O_{11}]$

(b) State two ways by which this equilibrium system could be upset.

(i) By DECREASING $[C_{12}H_{22}O_{11}]$ BY ADDING MORE H_2O SOLVENT

(ii) By INCREASING OR DECREASING THE TEMPERATURE

hemical Equilibrium

The previous examples were physical systems (ie. no chemical reactions were taking place). A typical chemical system is as follows.

g.1 $$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

Remember, that equilibrium can only exist in a closed system! That is at equilibrium some of all the species involved in the reaction exist. Also at equilibrium, the forward and reverse reaction rates are equal.

quilibrium Constant (K)

For any equilibrium reaction, there is an equilibrium constant (K).

$$K = \frac{\text{concentration of the products (at equilibrium)}}{\text{concentration of the reactants (at equilibrium)}}$$

Note: The value of K for a particular reaction can only be affected by TEMPERATURE ?.

for eg.1. $$K = \frac{[CO][H_2]}{[CO_2][H_2O]} = 0.11 \text{ (at 400° C)}$$

.2 $$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K = \frac{[HI]^2}{[H_2][I_2]} = 57 \text{ (at 425° C)}$$

4: What does a large K indicate about a particular reaction?

POSITION OF EQUILIBRIUM LIES TOWARDS THE PRODUCTS AS [PRODUCTS] > [REACTANTS]

Q5: Write K expressions for the following.
Note that solids and liquids do not form part of a K expression.

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

$K = \frac{[NO_2]^2}{[N_2O_4]}$ (0.21 at 100° C)

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

$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$ (0.11 at 470° C)

(iii) $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$K = [Ag^+][Cl^-]$ (1.7×10^{-10} at 25° C)

(iv) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

$K = [CO_2]$ (2.5×10^{-3} at 800° C)

Q6: For the following examples list the predominant species at equilibrium

(i)	$2SO_2 + O_2 \rightleftharpoons 2SO_3$	K =	85
(ii)	$C + H_2O \rightleftharpoons CO_2 + H_2$	K =	100
(iii)	$N_2O_4 \rightleftharpoons 2NO_2$	K =	8.75×10^{-2}
(iv)	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	K =	0.11

Most predominant species is/are

(i) SO_3 (ii) CO_2 & H_2

(iii) N_2O_4 (iv) N_2 & H_2

Le Chateliers Principle

Chemical systems that are in equilibrium can be easily affected by a change in conditions (e.g. pressure/concentration/tempterature).
Le Chateliers principle helps us predict the direction of the change. It can be stated as follows:

> If a change in conditions is made to a chemical system in equilibrium, then the system will adjust in such a way as to partially counteract the change.

Effect of Changing the Concentration

Suppose the concentration of a reactant is increased:
Le Chateliers principle would suggest that a change will take place to partially counteract this.
Hence some of the extra reactant will be consumed in re-establishing equilibrium.

g.3 $CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

If say CO_2 is added to the system when it is at equilibrium, then the system will adjust so as to favour the forward reaction (right). This will help to partially consume the extra CO_2 added.

'7: Predict the favoured reaction direction in the following cases.

System	Imposed Change	Direction Favoured
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	increase I_2	→
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH3_{(g)}$	increase NH_3	←
$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$	increase Ag^+	←
$MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(g)}$	increase $MgCO_3$	No EFFECT
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	decrease O_2	←
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	decrease NO	→

Effect of Changing Pressure/Volume.

In equilibrium systems involving gases, changing the volume can alter the pressure and concentration of all the species.

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

If this system is placed under higher pressure (or volume is reduced) the concentration of both N_2O_4 and NO_2 will be INCREASED.

The system will readjust to the left as this will help to partially reduce the concentration.

e.g.5 $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

In this case, changing the volume of the system will affect concentrations equally on both sides. Therefore, there will be no change in equilibrium position (although there will be a change in reaction rate).

Q8: Predict the favoured reaction direction in the following cases.

System	Volume Change	Direction Favoured
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	decrease	→
$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$	increase	→
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	increase	←
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	decrease	NO EFFECT
$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$	increase	No effect solution not affected by pressure.

Effect of Changing Temperature.

In considering temperature change it is best to include the heat of reaction as part of the equation. In this way heat can be treated as one of the "species" for the purpose of determining change in equilibrium.

e.g.6 For the reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

the heat of reaction (Δ H) is -113 kJ (ie. an exothermic reaction). Find the effect of increasing the temperature! Firstly rewrite the equation so as to include the heat of reaction.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} + 113 \text{ kJ.}$$

An increase in temperature will increase both the forward and reverse reaction rate but the equilibrium will shift to the left (ie. the extra heat can be consumed and satisfy Le Chateliers principle).

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$H_{2(g)} + I_{2(g)} + 52$ kJ $\rightleftharpoons 2HI_{(g)}$	decrease	←
$N_2O_{4(g)} + 57$ kJ $\rightleftharpoons 2NO_{2(g)}$	increase	→
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)} + 99$ kJ	increase	←
$CaCO_{3(s)} + 179$ kJ $\rightleftharpoons CaO_{(s)} + CO_{2(g)}$	decrease	←

Effect of Catalysts.

Catalysts effectively lower the activation energy for a reaction and hence help to increase both the forward and the reverse reaction rates.
Hence they do not effect equilibrium position.

Reaction Rates and Equilibrium Position.

These two aspects of any reaction should be treated independently although they may be related. The reaction rate of a reaction may increase but this does not necessarily favour products (as is often imagined).

Predicting Changes to a System - Complex Examples.

Some examples are best answered in tabular form.

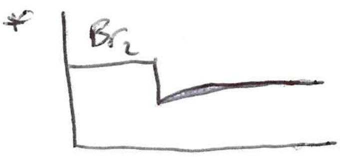
e.g.7 The following reaction is at equilibrium.

$$2NO_{(g)} \quad + \quad Br_{2(g)} \rightleftharpoons 2NOBr_{(g)}$$

How would the:
(a) Concentration of all the species
(b) The rates of forward and reverse reactions be affected if
 (i) Some NO is added to the system
 (ii) The concentration of $Br_{2(g)}$ is reduced.
 (iii) The pressure of the whole system is increased.

Imposed Change	[NO]	[Br2]	[NOBr]	F/Rate	R/Rate
Adding NO	Increase	DECREASE	INCREASE	INCREASE	INCREASE
Reducing [Br_2]	INCREASE	reduce the INCREASE x	DECREASE	DECREASE	DECREASE
Increasing Pressure	DECREASE	DECREASE	INCREASE	INCREASE	INCREASE

*Hint : For each imposed change consider what the final equilibrium position is tending to (from Le Chateliers principle).



Q10: Complete the following table which relates to the reaction shown.

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} + 564 \text{ kJ}$$

Imposed	$\overrightarrow{\text{F/Rate}}$	$\overleftarrow{\text{R/Rate}}$	$[CO_2]$	$[O_2]$
Adding CO	INCREASE	INCREASE	INCREASE	DECREASE
Increasing Temperature	INCREASE	INCREASE	DECREASE	INCREASE
Increasing Pressure	INCREASE	INCREASE	INCREASE	DECREASE
Reducing $[CO_2]$	DECREASE	DECREASE	reduce the INCREASE*	DECREASE

Q11: Add suitable headings to the following table to show how reaction rates and concentration of species are affected by increasing pressure, adding a catalyst, and removing $H_{2(g)}$.

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

IMPOSED	$\overrightarrow{\text{F/RATE}}$	$\overleftarrow{\text{R/RATE}}$	$[H_2O]$	$[CO]$	$[H_2]$
INCREASING PRESSURE	INCREASE	INCREASE	INCREASE	decrease	decrease
ADDING H_2O	INCREASE	INCREASE	increase the DECREASE	INCREASE	INCREASE
ADDING CO	INCREASE	INCREASE	INCREASE	increase the DECREASE	DECREASE
Adding Catalyst	increase	increase	no effect	no effect	no effect

Industrial Processes - Economic Factors.

In many industrial processes, reaction rates (or more specifically - the rate of attainment of equilibrium) and equilibrium yield are important considerations. The cost of providing desirable reaction conditions has also to be considered and very often a compromise must be made.

eg.8 The HABER process.

Ammonia gas is a very valuable industrial chemical and is produced by the following reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92 \text{ kJ}$$

To maximise yield and minimise cost the following is considered.

(i) **Temperature** — Low temperature gives the best yield, but this yield is achieved too slowly.

Compromise — Temperature 500 C gives an acceptable rate and yield

(ii) **Pressure** - High pressure gives the best yield, however both cost and danger increase with very high pressures.

Compromise — Pressure of about 350 Atm is used.

(iii) **Catalyst** — An iron/iron oxide catalyst has been found to increase rate of reaction.

We can summarise the factors involved in the HABER process as follows (please complete).

Variable Conditions		R/Rate	% Yield	Conditions Used
Temperature	High Low	fast slow	DECREASE INCREASE	COMPROMISE re kinetics
Pressure	High Low	→ ←	INCREASE DECREASE	HIGH PRESSURE
Catalyst	Yes No	FAST /	NO EFFECT	IRON CATALYST

Q:12 One of the reactions involved in the contact process for the manufacture of Sulfuric acid is as follows.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + 198\ kJ$$

Complete the table below to indicate the likely conditions that may be used to maximise the economic recovery of $SO_{3(g)}$

Variable Conditions		R/Rate	% Yield	Conditions Used
Temperature	High Low	fast slow	DECREASE INCREASE	COMPROMISE
Pressure	High Low	→ ←	INCREASE DECREASE	HIGH PRESSURE
Catalyst	Yes No	FAST /	NO EFFECT	VANADIUM(V) OXIDE

Q 8. FROM LAST PAGE (16)

(1) $NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightleftharpoons NH_{3(aq)} + H_2O_{(l)}$

(2) $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H_3O^+{}_{(aq)}$

WHEN THE 2 SOLUTIONS ARE ADDED TOGETHER THE H_3O^+ AND OH^- REACT FORMING H_2O ($H_3O^+ + OH^- \rightarrow 2H_2O$). THIS CAUSED THE POSITION OF EQUILIBRIUM IN (1) TO SHIFT LEFT TO PARTIALLY COUNTERACT THE REMOVAL OF OH^- IONS AND IN (2) TO SHIFT RIGHT TO PARTIALLY COUNTERACT REMOVAL OF $H_3O^+{}_{(aq)}$. ELECTRICAL CONDUCTIVITY INCREASES AS $[NH_4^+]$ AND $[CH_3COO^-]$ INCREASE

TRY THESE.

1. Ethane reacts with oxygen very slowly under normal conditons of temperature and pressure.

$$2C_2H_{6(g)} \quad + \quad 7O_2 \quad \longrightarrow \quad 4CO_{2(g)} \quad + \quad 6H_2O_{(g)}$$

Suggest three ways by which the rate of reaction could be increased.

(i) INCREASE TEMPERATURE (ii) INCREASE PRESSURE (iii) USE CATALYST.

kinetics more important

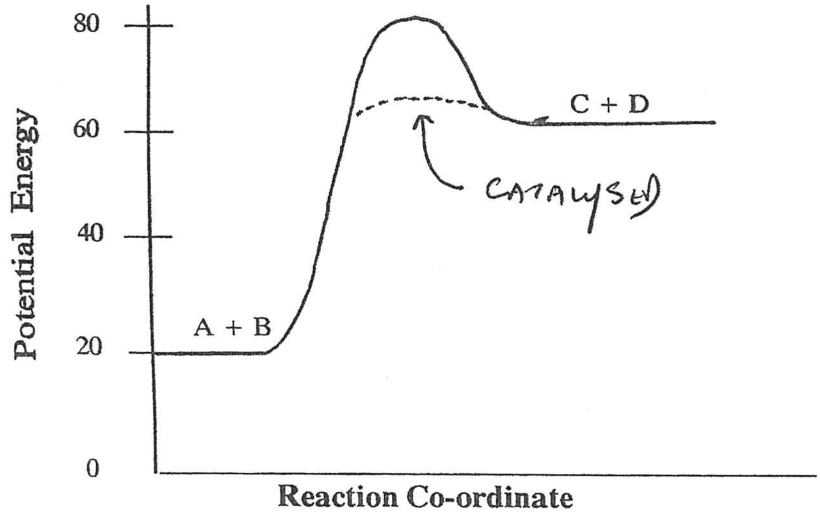
2. Some Carbon monoxide and Hydrogen gas were placed in a flask and allowed to come to equilibrium as follows:

$$CO_{(g)} + \quad H_{2(g)} \quad \rightleftharpoons \quad HCHO_{(g)}$$

While at equilibrium a very small amount of CO, labelled with radioactive carbon (C^{14}), was added. The amount added was so small as to not significantly alter the CO partial pressure. Several hours later (with the system still in equilibrium) some HCHO was removed and found to be contaminated with C^{14}. Explain clearly how this is possible.

EQUILIBRIUM IS DYNAMIC FORWARD & REVERSE REACTIONS ARE STILL TAKING PLACE.

3.



An energy profile diagram is shown above for the reaction

$$A \quad + \quad B \quad \longrightarrow \quad C \quad + \quad D$$

(a) For the forward reaction determine
- (i) The activation energy — 60
- (ii) The heat of reaction — +40
- (iii) What type of reaction it is — ENDOTHERMIC

(b) For the reverse reaction determine
- (i) The activation energy — 20
- (ii) The heat of reaction — −40

(c) (i) Draw in a possible catalysed pathway.
(ii) How will this affect heat of reaction? NO EFFECT

Acetic acid, which is a weak acid, ionises as follows.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

At equilibrium less than 1% of the acetic acid molecules have ionised and therefore the concentration of both H^+ and CH_3COO^- ions is very low.
The addition of some NaOH(aq) to the solution increases the concentration of the CH_3COO^-(aq) ions dramatically. Why is this? THE OH^- REACT WITH THE H^+ FORMING H_2O. THE POSITION OF EQUILIBRIUM SHIFTS TO PARTIALLY COUNTERACT THIS CHANGE, INCREASING H^+ IONS & SIMULTANEOUSLY CH_3COO^- IONS

Methanol gas can be broken down to carbon monoxide and hydrogen as follows:

$$CH_3OH_{(g)} \rightleftharpoons CO_{(g)} + 2H_{2(g)} \qquad \Delta H = +90 \text{ kJ}$$

Suggest conditions that would enhance this process.
LOW PRESSURE : FAVOURS SIDE WITH MORE MOLES
HIGH TEMPERATURE : FAVOURS THE ENDOTHERMIC PROCESS
REMOVAL OF ONE OF THE PRODUCTS.

The following reaction is at equlibrium.

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow 3H_{2(g)} + CO_{(g)} \qquad \Delta H = +206 \text{ kJ}$$

Set up a table to show what happens to reaction rate and concentration of each species when:
(i) H_2 gas is partially removed
(ii) The temperature is increased
(iii) The volume is reduced
(iv) A catalyst is added.

	RATE	$[CH_4]$	$[H_2O]$	$[H_2]$	$[CO]$
(i)	↓	↓	↓	↓	↑
(ii)	↑	↓	↓	↑	↑
(iii)	↑	↑	↑	↓	↓
(iv)	↑	N/A	N/A	N/A	N/A

When CO_2 dissolves in water the following equilibria exist.

① $CO_{2(g)} + H_2O_{(l)} \rightleftharpoons CO_{2(aq)}$

② $CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$

③ $HCO_3^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

Small amounts of each of the following substances were added (separately) to see the effect they would have on the apparent solubility of $CO_{2(g)}$ in H_2O.

(a) $NaOH_{(aq)}$ (b) $CH_3COOH_{(aq)}$

(c) $K_2CO_{3(s)}$ (d) $CaCl_{2(aq)}$

Predict the effect in each case and explain.

a) CO_2 (aq) ↑ : OH^- IONS REMOVE H^+ IONS ③ SHIFTS RIGHT CAUSING ② & ① TO SHIFT RIGHT

b) CO_2 (aq) ↓ : H^+ ADDED CAUSES ③ TO SHIFT LEFT CAUSING ② & ① TO SHIFT LEFT.

c) CO_3^{2-} (aq) REMOVE H^+ IONS, SAME AS a) AND CO_2 (aq) INCREASES.

d) NO EFFECT; $Ca^{2+}_{(aq)}$ & $Cl^-_{(aq)}$ DO NOT REACT WITH ANY OF THE SPECIES

Acetic acid and Ammonium hydroxide are respectively weak acid and base. Their solutions conduct electricity poorly. If the two solutions are combined however, they conduct electricity well! Use equilibrium reactions to explain. SEE PAGE 14