CHEMISTRY LEVEL 4C

(CHM 415115)

CHEMICAL EQUILIBRIUM

THEORY SUMMARY

&

REVISION QUESTIONS

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INDEX:

CHEMICAL EQUILIBRIUM

INTRODUCTION

Most of the chemical reactions that we have studied so far, have been ones that continue in the forward direction until one (or more) of the reactants has been consumed, at which point the chemical reaction stops.

For example, a piece of sodium metal reacts with water, forming aqueous sodium hydroxide and hydrogen gas and the reaction stops when the sodium is completely reacted. This reaction is not reversible! i.e.

$$2Na_{(s)} \quad + \quad 2H_2O_{(l)} \quad \rightarrow \quad 2NaOH_{(aq)} \quad + \quad H_{2(g)}$$
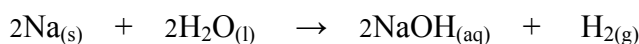
However, there are many reactions that are *reversible*; i.e. they can go in either direction.
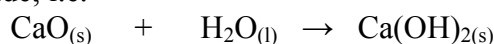
REVERSIBLE REACTIONS

Heating solid calcium hydroxide in a closed container results in some of it decomposing to form calcium oxide and water in the form of steam;
i.e.
$$Ca(OH)_{2(s)} \quad \rightarrow \quad CaO_{(s)} \quad + \quad H_2O_{(g)}$$

However, if solid calcium oxide is mixed with water, some will undergo a reaction to form calcium hydroxide; i.e.
$$CaO_{(s)} \quad + \quad H_2O_{(l)} \quad \rightarrow \quad Ca(OH)_{2(s)}$$

Reactions such as this that are reversible depending on the conditions are described as:

> 'EQUILIBRIUM SYSTEMS'

These type of reactions are shown as being reversible by writing the chemical equation using a double arrow notation such as:

$$Ca(OH)_{2(s)} \quad \rightleftharpoons \quad CaO_{(s)} \quad + \quad H_2O_{(l)}$$
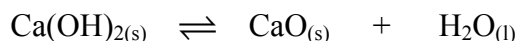
The interesting property about equilibrium systems is that they do not go to completion. This means that they come to an *apparent* stop before the limiting reagent is used up.

CHEMICAL EQUILIBRIUM

Consider the equilibrium system:

$$1N_{2(g)} \quad + \quad 3H_{2(g)} \quad \rightleftharpoons \quad 2NH_{3(g)}$$
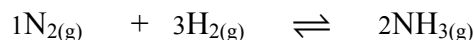
(i) If we mix one mole of nitrogen gas and three moles of hydrogen gas together in a closed container and allow them to react, some ammonia (NH_3) will be formed. However, even after a long period of time there will still be some N_2 and H_2 left unreacted. Neither reactant will have been consumed.

(ii) Conversely, commencing with pure ammonia gas (NH_3) and allowing it to decompose in a closed container, we find that N_2 and H_2 start forming but not all of the ammonia decomposes.

(iii) This is the typical outcome of equilibrium reactions; they don't go to completion and even after an extended period of time there are always **both** reactants and products present!

(iv) Chemical equilibrium reactions are very important in many areas, including:

- Industrial processes such as making ammonia and sulfuric acid.
- Acid ~ base reactions.
- Biochemical reactions.
- Manufacture of polymers and dyes.

Our concern is now to explain how and why equilibria come about and what factors determine how much of the reactants and products are present when the reaction appears to stop!

EXPLANATION OF EQUILIBRIUM

Consider the **closed** equilibrium system: $\quad A_{(g)} \quad \rightleftharpoons \quad B_{(g)}$

(i) Initially we have only reactant A present and the only reaction is the forward reaction.

(ii) Once some $B_{(g)}$ has formed, the reverse reaction starts to occur because the rate of the reverse reaction is a direct function of $[B_{(g)}]$

(iii) Thus the more B that is formed, the faster the reverse reaction takes place.

(iv) As $A_{(g)}$ is being used up, the rate of the forward reaction will decrease because the rate of the forward reaction is a direct function of $[A_{(g)}]$

(v) Eventually, at some critical concentration level, the rate of the forward reaction becomes exactly the same as the rate of the reverse reaction.

(vi) At this point we say that EQUILIBRIUM HAS BEEN ESTABLISHED!

(vii) The key point is that *at eqilibrium*;

THE RATE OF THE FORWARD REACTION ≡ THE RATE OF THE REVERSE REACTION

(viii) Equilibrium does NOT mean there are equal amounts of reactants and products. For example some equilibria involve equilibrium states where there may be almost all products and very small amounts of reactants and others may be quite the opposite. This is discussed later.

(ix) At equilibrium, because the rate of $A_{(g)}$ changing into $B_{(g)}$ is identical to the rate of $B_{(g)}$ changing back into $A_{(g)}$, we get the impression that the reaction has stopped occurring, but it hasn't! The two reactions continue to occur **BUT** they occur at the same rate! This is described as a dynamic balance. ('dynamic' means moving)

(x) At equilibrium, the $[A_{(g)}]$ will now be constant and so will the $[B_{(g)}]$ be constant, but they will not be the same value.

(xi) Because these concentrations are now fixed (constant) at equilibrium, the large-scale (macroscopic) properties of the system will now be constant; e.g. the concentration, colour, pressure, temperature, pH, radioactivity, ………..
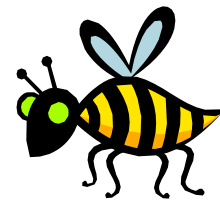
SUMMARY SO FAR

KEY POINT 1.
WE RECOGNISE THAT A CHEMICAL SYSTEM IS AT EQUILIBRIUM BY THERE BEING A CONSTANCY OF LARGE SCALE (MACROSCOPIC) PROPERTIES IN A CLOSED SYSTEM.

KEY POINT 2.
WE EXPLAIN THE EXISTENCE OF CHEMICAL EQUILIBRIUM BY THERE BEING A DYNAMIC BALANCE BETWEEN THE FORWARD AND REVERSE REACTIONS IN A CLOSED SYSTEM.

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"BEE-HIVE ANALOGY"

Consider a bee-hive situated in a region surrounded by flowers. We'll assume no bees disappear from the scene and no others enter from another hive and thus we can describe our system as *closed*.

Initially, before day-break, there are only bees in the hive and none is, as yet, out foraging for pollen and nectar. Now consider the sequence of changes:

| TIME OF DAY	BEES LEAVING HIVE PER MINUTE	BEES RETURNING TO HIVE PER MINUTE	EQUILIBRIUM EXISTS?
SUNRISE	500	0	NO
7.00 am	800	50	NO
8.00 am	1200	250	NO
9.00 am	1300	700	NO
10.00 am	1400	1000	NO
11.00 am	1300	1200	NO
Mid-day	1250	1250	YES

At mid-day, equilibrium has finally been achieved because we now have a dynamic balance between the two opposing processes of "bees leaving" and "bees returning".

Note that this *does not* mean that there are equal numbers of bees both in the hive and in the field.

Because this dynamic balance exists at mid-day, there will now be a constant number of bees both in the hive and in the surrounding gardens. This might give the impression that the processes of leaving and returning have ceased, but quite clearly, they haven't!
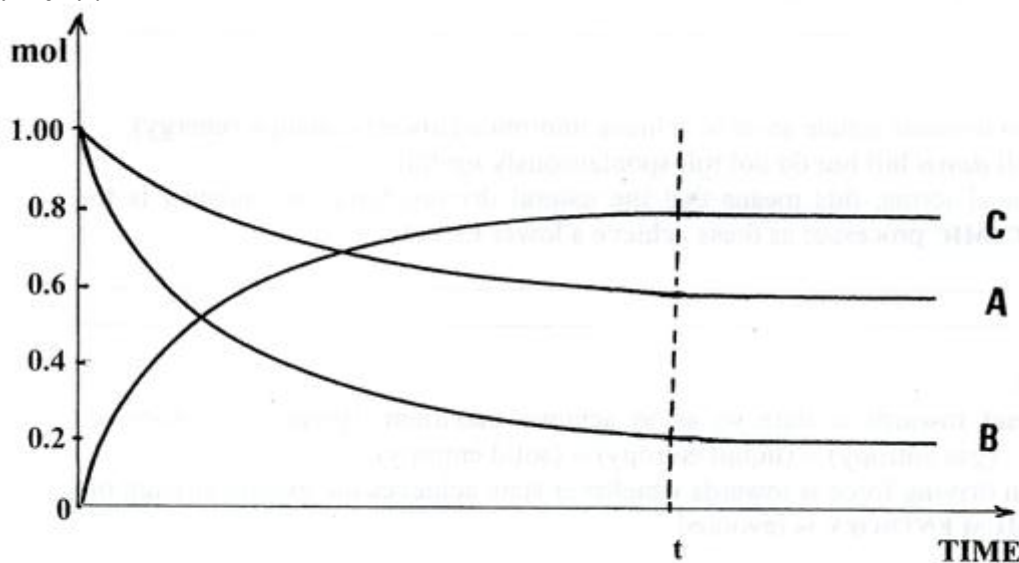
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GRAPHICAL REPRESENTATION

Consider the equilibrium system:

$$1A_{(g)} + 2B_{(g)} \rightleftharpoons 2C_{(g)}$$
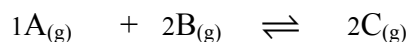
Suppose initially we place just 1.00 mole of $A_{(g)}$ and 1.00 mole of $B_{(g)}$ in a closed container.

At equilibrium suppose there is 0.80 mole of $C_{(g)}$ present.

The amounts of the three gases will change as shown below until equilibrium is achieved at time 't'.


NOTE:

(i) Initially there was only A and B present; 1.00 mol of each.

(ii) As the forward reaction proceeds, the amounts of A and B present decreased as they are progressively used up.

(iii) In accordance with the chemical equation's coefficients, B is used up at twice the rate at which A is consumed.

(iv) C is formed at the same rate as B is consumed.

(v) If 0.80 mol of C is present at equilibrium, it means that 0.80 mol of B must have reacted with 0.40 mol of A.

(vi) This means that the graph indicating the amount of B present has gone down by 0.80 mol from the initial and that the amount of A present has gone down by 0.40 mol from the initial.

(vii) As A and B are being used up initially, the rate of the forward reaction decreases and hence the magnitude of the slopes of the A and B graphs decrease.

(viii) When the graphs eventually level out (at time 't') this means that the relative amounts of A, B and C are no longer changing. This is explained by the attainment of a dynamic balance whereby the rate of the forward reaction is now identical to the rate of the reverse reaction.

THERMODYNAMICS & EQUILIBRIUM

Consider the following equilibrium system where the ***forward reaction*** is exothermic:

$$2SO_{2(g)} \quad + \quad 1O_{2(g)} \quad \rightleftharpoons \quad 2SO_{3(g)} \quad \Delta H = \text{NEGATIVE}$$
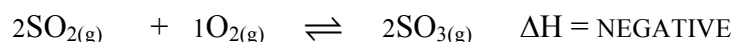
Why is this system an equilibrium system and not one where the reaction goes to completion?

From a thermodynamical viewpoint there are TWO naturally occurring tendencies that influence the outcomes of such systems.

TENDENCY 1.

All systems tend towards a state so as to achieve minimum (lower) enthalpy (energy).

e.g. boulders roll ***down*** hill but do not roll spontaneously ***up***-hill!

In thermochemical terms, this means that the natural driving force or tendency is to favour **EXOTHERMIC** processes as these achieve a lower E_P state.


TENDENCY 2.

All systems tend towards a state so as to achieve maximum (greater) disorder or entropy.

NOTE: (gas entropy) > (liquid entropy) > (solid entropy).

Thus the natural driving force is towards whichever state achieves the greater amount of gas; i.e. **MAXIMUM ENTROPY** is favoured.

In the sulfur dioxide/sulfur trioxide equilibrium system shown above, from a **MINIMUM ENTHALPY** viewpoint, the natural tendency is that the forward (exothermic) process is favoured; i.e.

MINIMUM ENTHALPY is achieved by $\quad 2SO_{2(g)} \quad + \quad 1O_{2(g)} \quad \rightarrow \quad 2SO_{3(g)}$
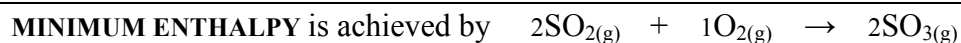
Conversely, from a **MAXIMUM ENTROPY** viewpoint, the natural tendency is that the reverse process is favoured because 3 moles of gas is a more disordered system (has greater entropy) than 2 moles of gas; i.e.

MAXIMUM ENTROPY is achieved by $\quad 2SO_{2(g)} \quad + \quad 1O_{2(g)} \quad \leftarrow \quad 2SO_{3(g)}$
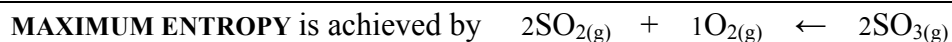
We thus see that in this particular reaction, the "minimum enthalpy" driving force favours the ***forward*** reaction occurring and yet the "maximum entropy" driving force favours the **reverse** reaction occurring.

In reality neither one of the two tendencies dominates and the system achieves a compromise between the two natural tendencies. This is why equilibrium reactions do not go to completion.

NOTE: As one raises the temperature of an equilibrium system, the system moves more and more towards the maximum entropy state.

> **IN SUMMARY:**
> **AN EQUILIBRIUM STATE REPRESENTS A COMPROMISE (OR BALANCE) BETWEEN THE TWO NATURALLY OCCURRING DRIVING FORCES TOWARDS MINIMUM ENTHALPY AND MAXIMUM ENTROPY.**
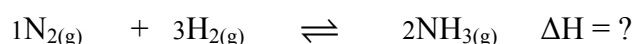
Q1. Consider the equilibrium system:
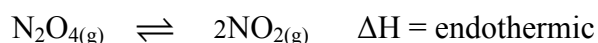
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H = \text{endothermic}$$

(i) Which reaction, the forward or the reverse direction, favours the system achieving a state of greater disorder (maximum entropy)? **(forward)**

(ii) Which reaction, the forward or the reverse direction, favours the system achieving a lower energy state (minimum enthalpy)? **(reverse)**

Q2. Consider the equilibrium system:

$$1N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = ?$$

(i) Which reaction, the forward or the reverse direction, favours the system achieving a state of greater disorder (maximum entropy)? **(reverse)**

(ii) In light of your answer to part (i) and the fact that this is an equilibrium system, which reaction, the forward or the reverse direction, favours the system achieving a lower energy state (minimum enthalpy)? **(forward)**

(iii) Is the forward reaction exothermic or endothermic? **(exothermic)**

Q3. Consider the equilibrium system involving the evaporation of water; i.e.

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)} \qquad \Delta H = \text{endothermic}$$
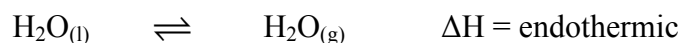
Although the evaporation of water is endothermic and thus not favoured in terms of achieving a state of minimum enthalpy (a lowered energy state), we all know that clothes etc dry by this evaporation process occurring.

Why does water tend to evaporate?

Q4. Consider the enthalpy and entropy changes occurring in the reaction between sodium metal and water.

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)} \qquad \Delta H = \text{exo}$$
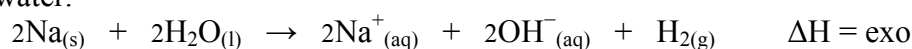
Why is this reaction not likely to represent an equilibrium system?

CHANGES TO EQUILIBRIA (LE CHATELIER'S PRINCIPLE)

Le Chatelier's Principle is a useful guide to predicting the effects of changes on the position of an equilibrium system.

In our experimental work we investigated the equilibrium system:

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$
(BLOOD RED)
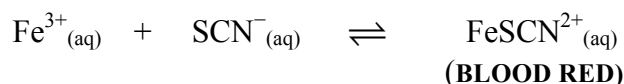
The position of equilibrium for this system can be easily followed by noting the change in the intensity of the red colour which indicates the relative amount of $FeSCN^{2+}_{(aq)}$ present at equilibrium.

(i) When additional $Fe^{3+}_{(aq)}$ was added to the system at equilibrium, the blood red colour became more intense. This tells us that there must have been some unreacted $SCN^-_{(aq)}$ ions present at equilibrium.
(ii) When additional $SCN^-_{(aq)}$ was added to the system at equilibrium, the blood red colour also became more intense. This tells us that there must have been some unreacted $Fe^{3+}_{(aq)}$ ions present at equilibrium.
(iii) When $Na_2HPO_{4(s)}$ was added to the system at equilibrium, the blood red colour faded. This tells us that some of the blood red $FeSCN^{2+}_{(aq)}$ ions originally present had decomposed.

These and other such experiments lead us to an general explanation which is referred to as LE CHATELIER'S PRINCIPLE; i.e.

> "If a system at equilibrium is subjected to an imposed change, then the position of equilibrium will adjust so as to partially counteract the imposed change".

Q5. For the ammonia synthesis equilibrium system:

$$1N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.0 \text{ kJ}$$

predict the effect on the position of equilibrium for the following imposed changes:
    (i) addition of more nitrogen gas ($N_{2(g)}$).
    (ii) removal of some hydrogen gas ($H_{2(g)}$).
    (iii) an increase in total pressure at constant temperature.
    (iv) an increase in temperature at constant pressure.
    (v) the addition of a catalyst.
    (vi) removal of some ammonia gas ($NH_{3(g)}$).

ANSWERS:

(i)   **CHANGE:** addition of more $N_{2(g)}$.
       EFFECT: system adjusts so as to partially remove $N_{2(g)}$.
       RESULT: forward reaction is favoured which consumes $N_{2(g)}$ and results in more $NH_{3(g)}$ being formed. (i.e. position of equilibrium shifts to the right)

(ii)   **CHANGE:** removal of some $H_{2(g)}$.
       EFFECT: system adjusts so as to partially replace $H_{2(g)}$.
       RESULT: reverse reaction is favoured which forms $H_{2(g)}$ and $N_{2(g)}$ and results in less $NH_{3(g)}$ being formed. (i.e. position of equilibrium shifts to the left).

(iii) **CHANGE:** increase in total pressure.
       EFFECT: system adjusts so as to partially decrease total pressure.
       RESULT: forward reaction is favoured which results in more $NH_{3(g)}$ being formed because 2 moles of NH_3 gas exerts less pressure than $(3 + 1) = 4$ moles of reactant gases (i.e. position of equilibrium shifts to the right).

(iv)   **CHANGE:** increase in temperature.
       EFFECT: system adjusts so as to partially decrease temperature.
       RESULT: the endothermic reverse reaction is favoured because this brings about a decrease in temperature. This results in less $NH_{3(g)}$ being formed;
       (i.e. position of equilibrium shifts to the left)

(v)   **CHANGE:** addition of a catalyst.
       RESULT: the catalyst has ***no effect*** on the position of equilibrium because it speeds up both the forward and reverse reactions equally.
       The addition of a catalyst does however result in the attainment of equilibrium being achieved more quickly.

(vi)   **CHANGE:** removal of some $NH_{3(g)}$.
       EFFECT: system adjusts so as to partially replace $NH_{3(g)}$.
       RESULT: forward reaction is favoured which forms $NH_{3(g)}$ and results in less $H_{2(g)}$ and $N_{2(g)}$ being present. (i.e. position of equilibrium shifts to the right).

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EQUILIBRIUM CHANGES
LE CHATELIER'S PRINCIPLE
GRAPHICAL REPRESENTATION OF CHANGES

Changes to equilibrium systems are often represented by sketch graphs of concentration or amounts of species versus time.

Moles or molarity are normally on the vertical ("y") axis and time on the horizontal ("x") axis.

With these graphs, there are some common features that you need to be familiar with; these include:

- *Horizontal* or 'flat' sections of the graph represent constant concentrations; i.e. equilibium exists.

- A sudden increase in *all* gaseous component's concentrations usually indicates that there has been a rapid decrease in volume caused by *pressure increase* and thus concentrations all increased momentarily.

- A sudden decrease in *all* gaseous component's concentrations usually indicates that there has been a rapid increase in volume caused by *pressure decrease* and thus concentrations all decreased momentarily.

- A single component's concentration suddenly rising or (falling) usually indicates that there has been a rapid addition (removal) of this component.

- A gradual change in *all* component concentrations (some rising and some falling) is usually associated with a change of temperature where:
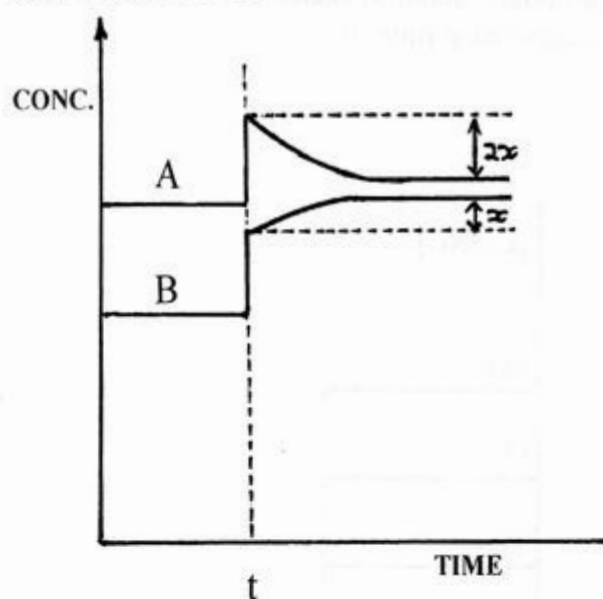
> (i) a temperature **increase** favours the ENDOTHERMIC direction.
>
> (ii) a temperature **decrease** favours the EXOTHERMIC direction.

- The addition of a catalyst results in the gradient (slope) being steeper than would be the case with no catalyst present.
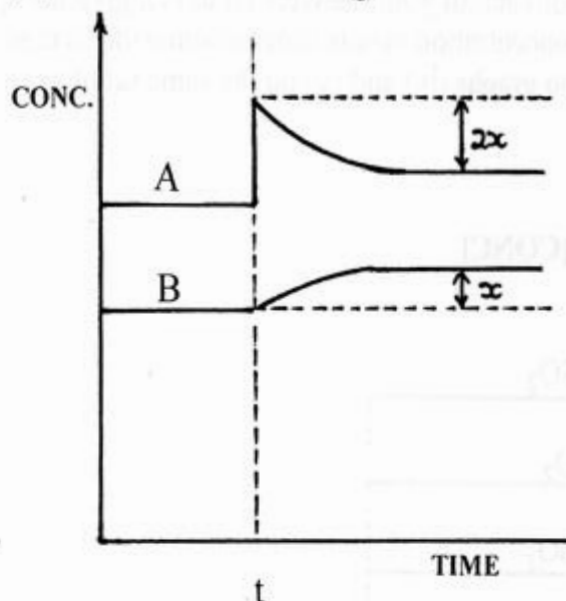
EXAMPLE.

Consider the equilibrium system: $2A_{(g)} \rightleftharpoons 1B_{(g)}$ $\Delta H = EXO$

In each of the following graphical representations, an imposed change (as specified) is imposed at time 't'. The system was at equilibrium before time 't' and each separate graph shows the effect of the imposed change on the system after time 't'.
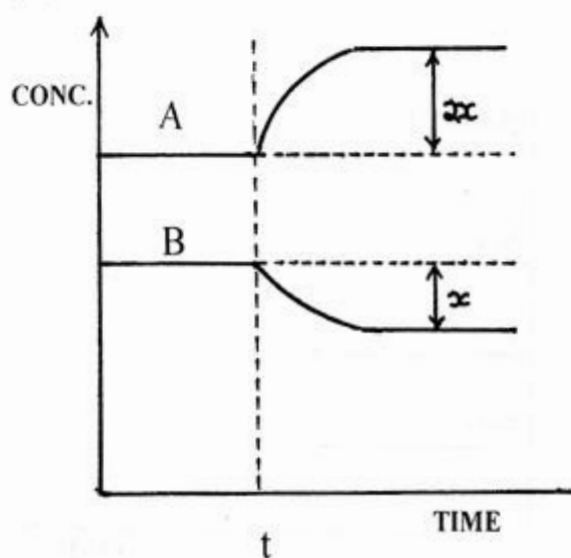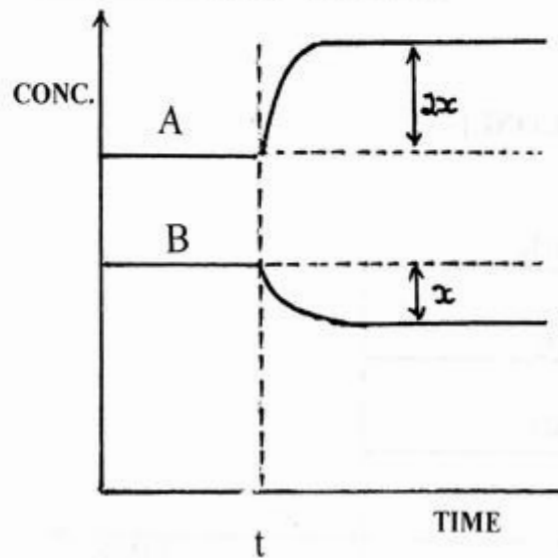
(i) SUDDEN PRESSURE INCREASE

(ii) RAPID ADDITION OF $A_{(g)}$

(iii) TEMPERATURE INCREASE

(iv) TEMP. INCREASE + CATALYST

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Q6. Consider the equilibrium system involving the oxidation of sulfur dioxide.

$$2SO_{2(g)} + 1O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -192 \text{ kJ}$$

What would be the effect on the position of equilibrium if:
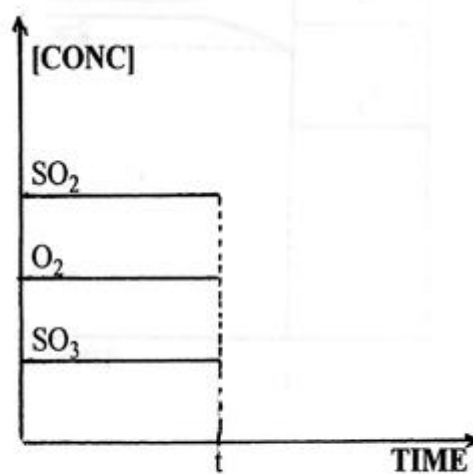
(i) the total pressure was decreased at constant temperature?
(ii) the temperature was increased at constant pressure?
(iii) the temperature was decreased at constant pressure?
(iv) the partial pressure of $SO_{2(g)}$ (p_{SO_2}) was increased?
(v) (p_{SO_2}) was increased with a catalyst present too ?

For each of your answers (i) to (v), give the appropriate graphical sketch of concentration versus time. Assume the change is imposed at time "t".
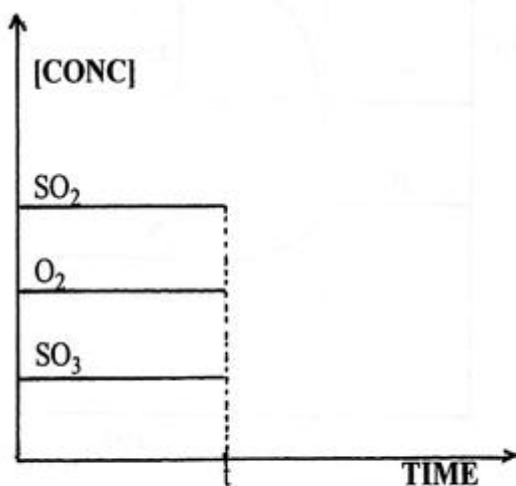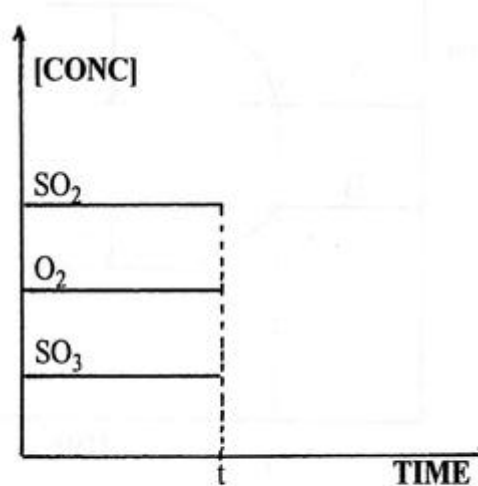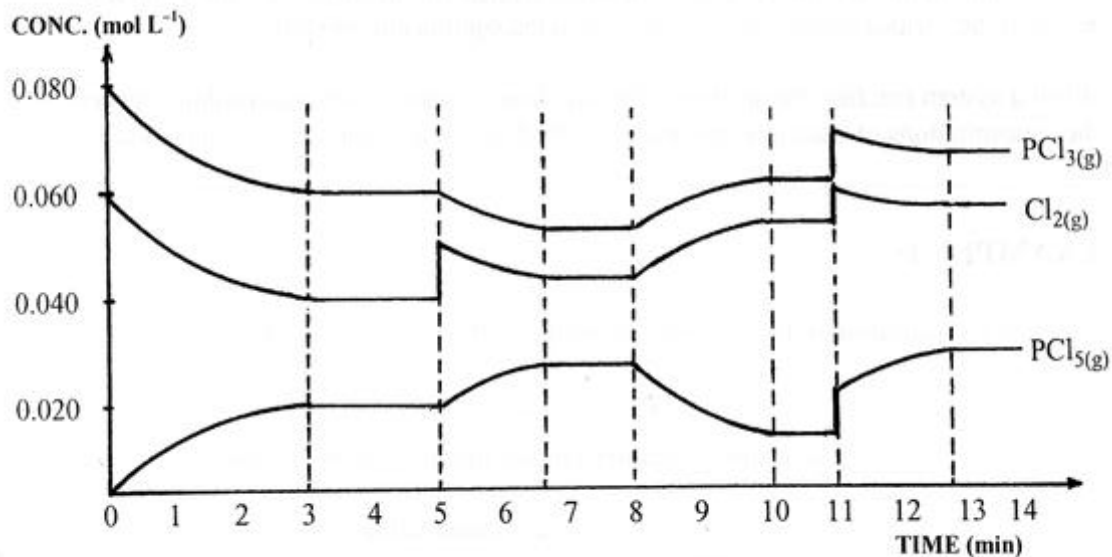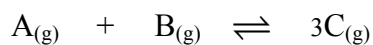Do graphs (iv) and (v) on the same set of axes.

(i)

(ii)

(iii)

(iv) & (v)

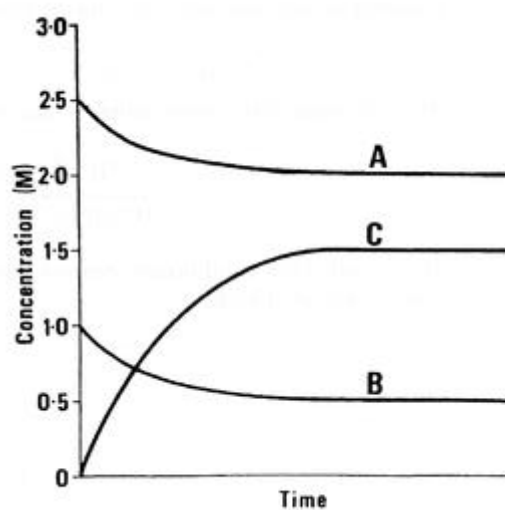Q7. Consider the following graphical representation of concentration versus time for the equilibrium system:

$$PCl_{3(g)} \quad + \quad Cl_{2(g)} \quad \rightleftharpoons \quad PCl_{5(g)} \qquad \Delta H = -92.5 \text{ kJ}$$

CONC. (mol L^{-1})

(i) When was equilibrium first established?
(ii) What change was imposed at time = 5 minutes?
(iii) What change was imposed at time = 8 minutes?
(iv) What change was imposed at time = 11 minutes?
(v) Using the data for the 4 minute mark, find the value of K_c at the temperature concerned. (K_c - see p.16)
(vi) Indicate on the graph above, how the curves may have differed if a catalyst had been introduced to the system at time 8 minutes.

Q8. Gaseous species A and B react in an equilibrium system as shown by the equation:

$$A_{(g)} \quad + \quad B_{(g)} \quad \rightleftharpoons \quad 3C_{(g)}$$

The graphs to the right show the changes in concentration occurring immediately after 2.50 mol of A and 1.00 mol of B were mixed in a 1.00 L container.
(i) On the graph's time axis, indicate when equlibrium was first established.
(ii) Use the data to determine the value of K_c at the temperature concerned.
(K_c - see p.16)   **(K_c = 3.38)**

15

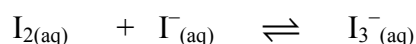# THE EQUILIBRIUM CONSTANT (K_c)

Up to this point we have only considered the qualitative aspects of chemical equilibrium. In this section we will learn how chemists can make predictions about *how much* of the various components are present in the equilibrium mixture.

When a system reaches chemical equilibrium, there is quantitative relationship between the concentrations of reactants and products which is constant for a given temperature.

EXAMPLE 1:

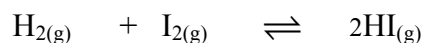Consider the equilibrium involving the formation of the brown tri-iodide ion:

$$I_{2(aq)} + I^-_{(aq)} \rightleftharpoons I_3^-{}_{(aq)}$$

At $25^{\circ}C$ when this system achieves equilibrium, we find that the expression

$$\frac{[I_3^-{}_{(aq)}]}{[I_{2(aq)}][I^-_{(aq)}]} \quad \text{has a constant value of 723 L mol}^{-1}.$$

This is called the equilibrium constant expression for this chemical equilibrium system and is designated by K_c.

EXAMPLE 2:

Consider the equilibrium involving the formation of hydrogen iodide:

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

At $491^{\circ}C$ when this system achieves equilibrium, we find that the expression

$$\frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]} \quad \text{has a constant value of 45.5}$$

This is called the equilibrium constant expression for this chemical equilibrium system and is designated by K_c.

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GENERAL CASE:

Consider the equilibrium involving reactants A and B and products C and D where w, x, y and z are the coefficients in the equation:
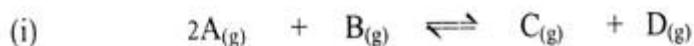
$$xA_{(g)} + yB_{(g)} \rightleftharpoons wC_{(g)} + zD_{(g)}$$

When this system achieves equilibrium at a given temperature, we find that the expression

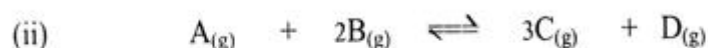$$\frac{[C_{(g)}]^w[D_{(g)}]^z}{[A_{(g)}]^x[B_{(g)}]^y}$$

has a constant value irrespective of the amounts of A, B C and D that were initially present. This constant is called the equilibrium constant and represented by K or more correctly K_c.

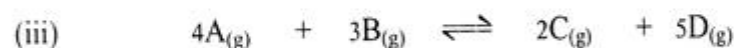The subscript 'c' indicates that concentrations at equilibrium are measured in mol L^{-1}

Q9. Give the equilibrium constant expression for the following equilibrium equations:

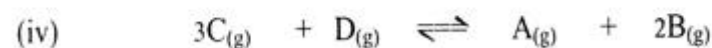(i) $\quad 2A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$

ANS. $\dfrac{[C_{(g)}][D_{(g)}]}{[A_{(g)}]^2[B_{(g)}]}$

(ii) $\quad A_{(g)} + 2B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}$

ANS. $\dfrac{[C_{(g)}]^3[D_{(g)}]}{[A_{(g)}][B_{(g)}]^2}$

(iii) $\quad 4A_{(g)} + 3B_{(g)} \rightleftharpoons 2C_{(g)} + 5D_{(g)}$

ANS. $\dfrac{[C_{(g)}]^2[D_{(g)}]^5}{[A_{(g)}]^4[B_{(g)}]^3}$

(iv) $\quad 3C_{(g)} + D_{(g)} \rightleftharpoons A_{(g)} + 2B_{(g)}$

ANS. $\dfrac{[A_{(g)}][B_{(g)}]^2}{[C_{(g)}]^3[D_{(g)}]}$

EQUILIBRIUM CONSTANT (K$_c$)
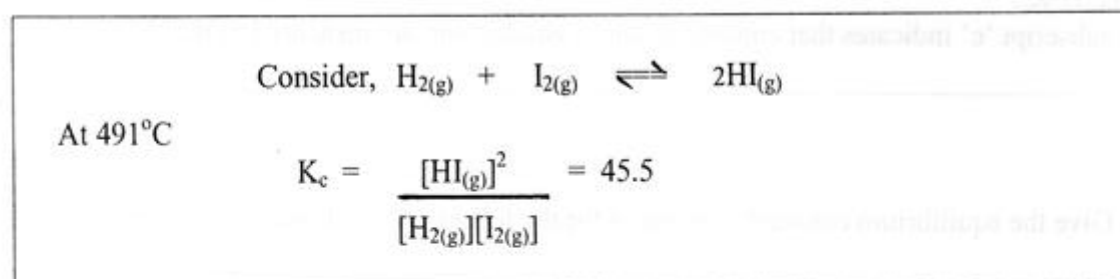# IMPORTANT NOTES

(i) K$_c$ is always written with product terms on the numerator and reactant terms on the denominator.

(ii) Each concentration term is raised to the power of the coefficient in the equilibrium equation; e.g if the equation has 3A$_{(g)}$ then K$_c$ will involve $[A_{(g)}]^3$ .... etc
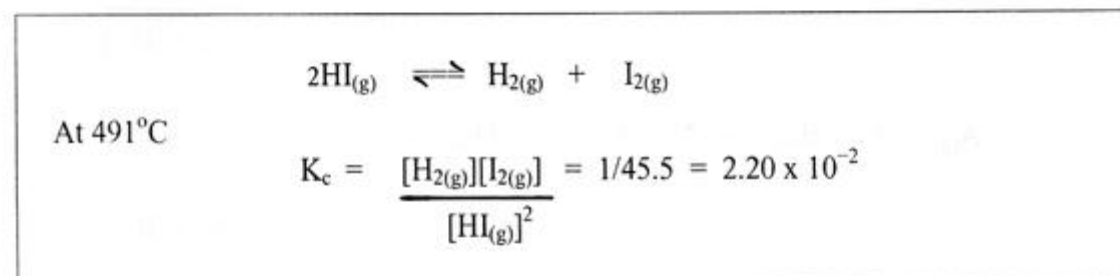
(iii) K$_c$ values must be quoted for a particular temperature because the value of K$_c$ for any given equilibrium system varies with temperature.

(iv) K$_c$ values must be written with respect to a particular equation because reversing the equation or altering the coefficients will change the value of the constant.
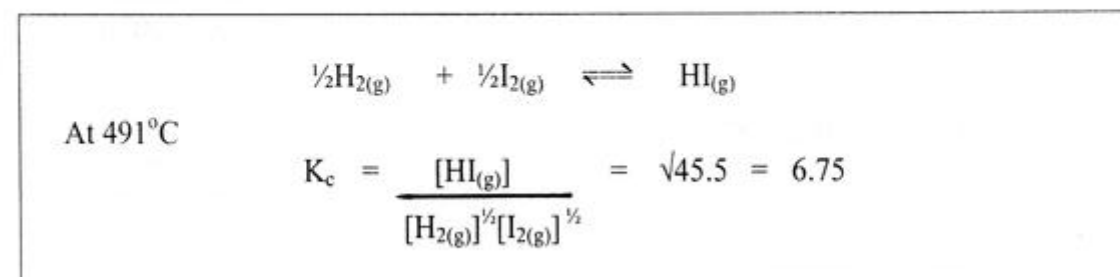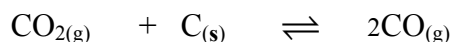e.g.

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

At 491°C

$$K_c = \frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]} = 45.5$$

But, for the reverse equation:

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

At 491°C

$$K_c = \frac{[H_{2(g)}][I_{2(g)}]}{[HI_{(g)}]^2} = 1/45.5 = 2.20 \times 10^{-2}$$

And for the half-coefficient equation:

$½H_{2(g)} + ½I_{2(g)} \rightleftharpoons HI_{(g)}$

At 491°C

$$K_c = \frac{[HI_{(g)}]}{[H_{2(g)}]^{½}[I_{2(g)}]^{½}} = \sqrt{45.5} = 6.75$$

(v) Because the concentration of any given solid is itself a constant at a certain temperature, we do not include *solids* in the equilibrium expression.

Thus for the equilibrium system:

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

The equilibrium constant expression is:

(vi) If the concentrations of gaseous species are measured as partial pressures rather than mol L^{-1}, the equilibrium constant is of identical format except that it is called K_P.

$$K_c = \frac{[CO_{(g)}]^2}{[CO_{2(g)}]} \qquad \text{because } [C_{(s)}] = \text{constant}$$

(vii) The units of K_c will be (mol L^{-1})^n where n is the (sum of numerator coefficients) minus (the sum of denominator coefficients)

e.g. $$1N_{2(g)} \ + \ 3H_{2(g)} \ \rightleftharpoons \ 2NH_{3(g)}$$

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3} \ \frac{(\text{mol } L^{-1})^2}{(\text{mol } L^{-1})^4} \quad \text{Thus } K_c \text{ will have units of } (\text{mol } L^{-1})^{-2}$$

(viii) The numerical values of K_c can range between zero and plus infinity.

(ix) The numerical value of K_c gives an indication of the extent of the forward reaction.

For example, consider: $A_{(g)} \ \rightleftharpoons \ B_{(g)}$

The equilibrium constant expression is: $$K_c = \frac{[B_{(g)}]}{[A_{(g)}]} \ \dots\dots\dots\dots\dots\dots\dots *$$

If K_c is a very large number, e.g. $K_c = 10^7$, this means that the denominator in (*) must be nearly zero and thus, at equilibrium there is practically no $A_{(g)}$ present.

i.e. K_c is a very large ➜ reaction almost goes to completion in the forward direction.

If K_c is practically zero, e.g. $K_c = 10^{-7}$, this means that the numerator in (*) must be nearly zero and thus, at equilibrium there is practically no $B_{(g)}$ present.

i.e. K_c is nearly zero ➜ reaction hardly occurs in the forward direction.

(x) The reaction quotient (Q) has the *same* concentration terms as the K_c expression but can be used for concentrations other than at equilibrium.

(xi) The value of Q indicates the direction in which a reacting system will move so as to establish equilibrium. i.e.

- If $Q < K_c$, then the forward reaction will be favoured.

- If $Q > K_c$, then the reverse reaction will be favoured.

- If $Q = K_c$, then the system is at equilibrium.

(xii) For gaseous equilibria, pressure changes can alter the *position* of equilibrium but the value of K_c is not altered unless there is a change in temperature.

EFFECT OF TEMPERATURE CHANGES ON K_c

1. Consider the equilibrium system:

$$A_{(g)} \rightleftharpoons B_{(g)} \quad \Delta H = \text{exothermic}$$

Where there is a ΔH term given, it always relates to the *forward* direction, i.e. in this case, the reaction $A \rightarrow B$ is exothermic.

For this system, $\quad\quad\quad\quad\quad K_c = [B_{(g)}]/[A_{(g)}]$

Raising the temperature will, in accordance with L.C.P. cause the reverse reaction to be favoured and thus $[A_{(g)}]$ increases and $[B_{(g)}]$ decreases making K_c smaller.

Conversely, lowering the temperature will, in accordance with L.C.P. cause the forward reaction to be favoured and thus $[A_{(g)}]$ decreases and $[B_{(g)}]$ increases making K_c larger.
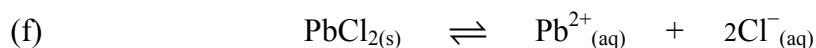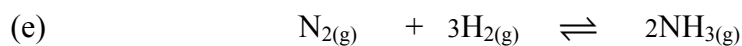
2. Consider the equilibrium system:

$$X_{(g)} \rightleftharpoons Y_{(g)} \quad \Delta H = \text{endothermic}$$

In this case, the reaction $X \rightarrow Y$ is endothermic.

For this system, $\quad\quad\quad\quad\quad K_c = [Y_{(g)}]/[X_{(g)}]$

Raising the temperature will, in accordance with L.C.P. cause the forward reaction to be favoured and thus $[Y_{(g)}]$ increases and $[X_{(g)}]$ decreases making K_c larger.
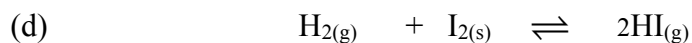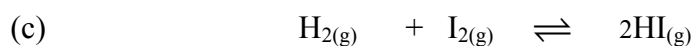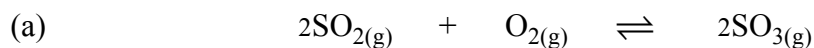
Conversely, lowering the temperature will, in accordance with L.C.P. cause the reverse reaction to be favoured and thus $[X_{(g)}]$ increases and $[Y_{(g)}]$ decreases making K_c smaller.
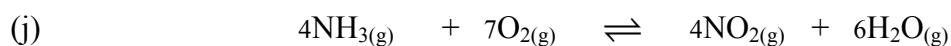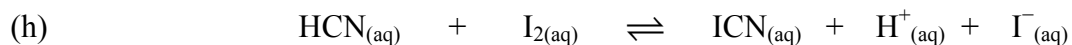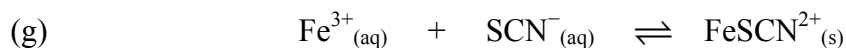
SUMMARY OF TEMPERATURE EFFECTS ON K_c

TEMPERATURE CHANGE	$A_{(g)} \rightleftharpoons B_{(g)}$ $\Delta H = $ EXO	$X_{(g)} \rightleftharpoons Y_{(g)}$ $\Delta H = $ ENDO
TEMPERATURE IS INCREASED	K_c DECREASES	K_c INCREASES
TEMPERATURE IS DECREASED	K_c INCREASES	K_c DECREASES

EQUILIBRIUM CONSTANT EXPRESSIONS

Q10. For each of the following equilibrium systems write the correct form for the equilibrium constant expression (K_c) and give the correct units.
(Write your answers in the spaces provided)

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

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

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

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

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

(f) $PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

(g) $\qquad$ $Fe^{3+}_{(aq)}$ + $SCN^-_{(aq)}$ $\rightleftharpoons$ $FeSCN^{2+}_{(s)}$

(h) $\qquad$ $HCN_{(aq)}$ + $I_{2(aq)}$ $\rightleftharpoons$ $ICN_{(aq)}$ + $H^+_{(aq)}$ + $I^-_{(aq)}$

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

(j) $\qquad$ $4NH_{3(g)}$ + $7O_{2(g)}$ $\rightleftharpoons$ $4NO_{2(g)}$ + $6H_2O_{(g)}$

NOTE:
In *aqueous* equilibria where *liquid* water is a reactant or product, the $[H_2O_{(l)}]$ is not included in the equilibrium expression because this concentration term is effectively a constant also. (Pure water $= 1000$ g L^{-1} which corresponds to $[H_2O_{(l)}] = 55.5$ mol L^{-1})

Q11. For each of the following equilibrium reactions write the correct form for the equilibrium constant expression (K_c) and give the correct units.
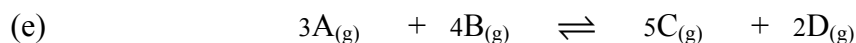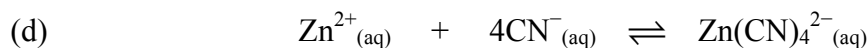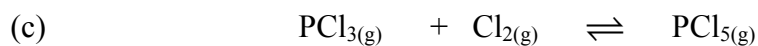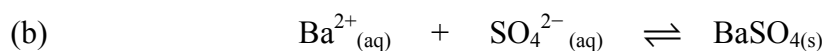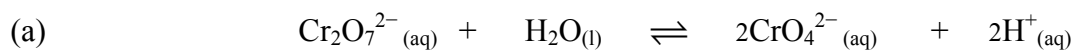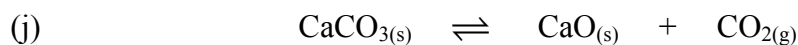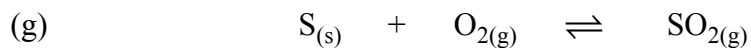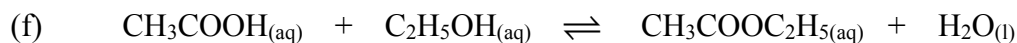(Write your answers in the spaces provided)

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

(b) $\qquad$ $Ba^{2+}_{(aq)}$ + $SO_4^{2-}{}_{(aq)}$ $\rightleftharpoons$ $BaSO_{4(s)}$

(c) $\qquad$ $PCl_{3(g)}$ + $Cl_{2(g)}$ $\rightleftharpoons$ $PCl_{5(g)}$

(d) $\qquad$ $Zn^{2+}_{(aq)}$ + $4CN^-_{(aq)}$ $\rightleftharpoons$ $Zn(CN)_4^{2-}{}_{(aq)}$

(e) $\qquad$ $3A_{(g)}$ + $4B_{(g)}$ $\rightleftharpoons$ $5C_{(g)}$ + $2D_{(g)}$

(f) $CH_3COOH_{(aq)}$ + $C_2H_5OH_{(aq)}$ $\rightleftharpoons$ $CH_3COOC_2H_{5(aq)}$ + $H_2O_{(l)}$

(g) $S_{(s)}$ + $O_{2(g)}$ $\rightleftharpoons$ $SO_{2(g)}$

(h) $I_{2(s)}$ $\rightleftharpoons$ $I_{2(g)}$

(i) $I_{2(g)}$ $\rightleftharpoons$ $2I_{(g)}$

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

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Q12. Given that the value of the equilibrium constant K_c for the equilibrium equation:
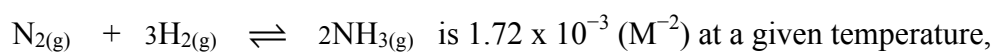
$N_{2(g)}$ + $3H_{2(g)}$ $\rightleftharpoons$ $2NH_{3(g)}$ is 1.72×10^{-3} (M^{-2}) at a given temperature,

find the value of the equilibrium constant K_c for the equilibrium equation:

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

(581 M^2)

(ii) $½N_{2(g)}$ + $3/2H_{2(g)}$ $\rightleftharpoons$ $NH_{3(g)}$

(4.15 x 10^{-2} M^{-1})

(iii) $NH_{3(g)}$ $\rightleftharpoons$ $½N_{2(g)}$ + $3/2H_{2(g)}$

(24.1 M)

(iv) $4NH_{3(g)}$ $\rightleftharpoons$ $2N_{2(g)}$ + $6H_{2(g)}$
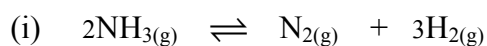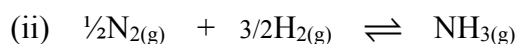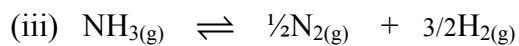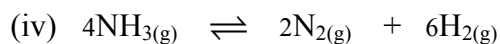
(3.38 x 10^5 M^4)

CALCULATING THE VALUE FOR K_c
"I.C.E. DIAGRAMS"

Consider the equilibrium system:

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$
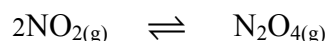
Suppose that initially 1.60 mole of NO_2 gas is placed in a 40.0 L container at T°C. After a given period of time, the system has achieved equilibrium and it is found that there is now 0.20 mole of N_2O_4 gas present.
What is the value of K_c for this equilibrium reaction at T°C?

ANSWER:

A good technique for solving such equilibrium problems like this is to use an "I.C.E." diagram where the acronym stands for **i**nitial, **c**hange and **e**quilibrium.

i.e.

moles	$2NO_{2(g)}$ $\rightleftharpoons$	$N_2O_{4(g)}$
INITIAL	1.60	0.00
CHANGE	–0.40	+0.20
EQUILIBRIUM	1.20	0.20

The filling in of the ICE diagram involves the following steps:

STEP 1.
Enter the **INITIAL** numbers of moles of the species present and use 0.00 for species that were not present at the beginning.

STEP 2.
Enter the number of moles of whichever species is known to be present at **EQUILIBRIUM.**

STEP 3.

Determine the **CHANGE** that has occurred for the species that is known both initially and at equilibrium.
If this species has increased in amount, use a (+) change value and if the amount has decreased use a (−) change value.

STEP 4.

Fill in the **CHANGE** row using mole amounts that correspond to the coefficients in the equilibrium equation remembering that a (+) change value is used for species that are being *formed* and a (−) change value is used for species being ***used*** up.

STEP 5.

Using the values at **EQUILIBRIUM**, calculate the concentration of the species present in units of mol L^{-1} by dividing by the volume in litres which in this case is 40.0 L.
i.e.

$$\text{at equilibrium;} \qquad [NO_{2(g)}] = 1.20/40.0$$

$$= 0.0300 \text{ mol } L^{-1}$$

$$[N_2O_{4(g)}] = 0.20/40.0$$

$$= 0.0050 \text{ mol } L^{-1}$$
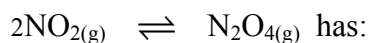
STEP 6.

Using the molarities at **EQUILIBRIUM**, substitute these into the expression for K_c and calculate the value.

i.e.
$$K_c = \frac{[N_2O_{4(g)}]}{[NO_{2(g)}]^2}$$

$$= \frac{0.0050 \text{ mol } L^{-1}}{(0.0300 \text{ mol } L^{-1})^2}$$

$$= 5.6 \text{ L mol}^{-1} \quad \text{(to 2 sig. figs)}$$

Thus, at T^oC, the equilibrium system

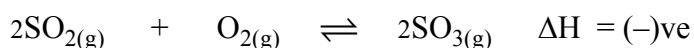$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \text{ has:}$$

$$K_c = 5.6 \text{ L mol}^{-1}$$

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THE EQUILIBRIUM CONSTANT
REVISION QUESTIONS

Q13. Consider the equilibrium system:

$$2SO_{2(g)} \quad + \quad O_{2(g)} \quad \rightleftharpoons \quad 2SO_{3(g)} \quad \Delta H = (-)ve$$

At $600^{\circ}C$ this equilibrium system has $K_c = 4.51$ L mol^{-1}.

(a) Write the expression for the equilibrium constant.

(b) Why are the units for this K_c value L mol^{-1}?

(c) If the total pressure of the system was raised but the temperature maintained at $600^{\circ}C$, what effect would this have on:

   (i) the position of equilibrium?

(shifts to the right)

   (ii) the value of K_c for this equilibrium system? Explain carefully.

(K_c unaltered)

(d) If the temperature was raised to $700^{\circ}C$, what effect would this have on the value of K_c for this equilibrium system? Explain carefully.

(K_c decreases)

(e) A particular mixture of the three gases at $600^{\circ}C$ has the following composition in terms of gas concentrations:

$$[SO_{2(g)}] = 0.125 \text{ mol L}^{-1}.$$

$$[O_{2(g)}] = 0.350 \text{ mol L}^{-1}.$$

$$[SO_{3(g)}] = 0.0381 \text{ mol L}^{-1}.$$

Is this mixture at equilibrium? Explain your answer.

(not equilibrium)

(f) Another mixture of the three gases at 600°C has reached equilibrium and two of the gas concentrations present are:

$$[SO_{2(g)}] = 0.0652 \text{ mol L}^{-1}.$$

$$[SO_{3(g)}] = 0.0301 \text{ mol L}^{-1}.$$

Calculate the $[O_{2(g)}]$ at equilibrium assuming that $K_c = 4.51 \text{ L mol}^{-1}$.
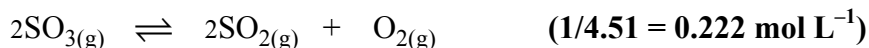**(0.0473 mol L^{-1})**

(g) In terms of the ***position*** of equilibrium what conditions of temperature and pressure would favour the maximum production of $SO_{3(g)}$?
(high pressures and low temperatures)

(h) Although a ***low*** temperature is favoured to maximise the production of $SO_{3(g)}$, why does the industrial production of $SO_{3(g)}$ use a high temperature?

(i) Apart from high temperatures and pressures, what other methods are employed to maximise the production rate of $SO_{3(g)}$?

(j) Calculate the numerical value of K_c at 600°C for the equilibrium system:

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)} \qquad \textbf{(1/4.51 = 0.222 mol L}^{-1}\textbf{)}$$

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Q14. For the equilibrium system: $\qquad Br_{2(aq)} + Br^-_{(aq)} \rightleftharpoons Br_3^-_{(aq)}$

at 25°C the value of the equilibrium constant is $K_c = 17.9 \text{ L mol}^{-1}$.

(i) What is the value of K_c for: $\quad Br_3^-_{(aq)} \rightleftharpoons Br_{2(aq)} + Br^-_{(aq)}$ at 25°C?
(0.0559 mol L^{-1})

(ii) An equilibrium mixture at 25°C has: $\qquad [Br_{2(aq)}] = 0.026 \text{ mol L}^{-1}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad [Br^-_{(aq)}] = 0.047 \text{ mol L}^{-1}$

What is the corresponding $[Br_3^-_{(aq)}]$?

([Br$_3^-_{(aq)}$] = 0.022 mol L^{-1})

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Q15. The equilibrium system $Cl_{2(g)} + CO_{(g)} \rightleftharpoons COCl_{2(g)}$ at 125°C has an equilibrium constant $K_c = 4.0 \times 10^5 \text{ L mol}^{-1}$. What conclusion can be drawn from the value of K_c being so large?
(reaction practically goes to completion)

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Q16. The equilibrium system $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ at 125°C has an equilibrium constant $K_c = 1.0 \times 10^{-5}$. What conclusion can be drawn from the value of K_c being nearly zero?
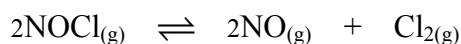
(practically no forward reaction occurs)

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Q17. Consider the equilibrium system:
$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
0.0800 mole of $PCl_{5(g)}$ is initially placed in a 1.00 L reaction vessel. When equilibrium is established at 250°C, the concentrations of $PCl_{3(g)}$ and $Cl_{2(g)}$ are both found to be 0.0406 mol L^{-1}. Calculate the value of K_c at 250°C.

($K_c = 0.0418$ mol L^{-1})

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Q18. The compound nitrosyl chloride NOCl decomposes into nitric oxide and chlorine as shown by the equilibrium equation:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

0.500 mole of $NOCl_{(g)}$ was placed in a 1.00 L vessel and heated to 500 K. When equilibrium had been established, the $[Cl_{2(g)}]$ was found to be 0.035 mol L^{-1}. Calculate the value of K_c at 500 K.　　　　　　**($K_c = 9.3 \times 10^{-4}$ mol L^{-1})**

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

Q19. Consider the equilibrium: $Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$.
"Limewater" is a saturated solution of calcium hydroxide which means that the system is at equilibrium. Because the equilibrium involves a solid, the equilibrium constant is written as K_s rather than K_c but remember the solid concentration term doesn't appear in the equilibrium expression for K_s.
  (i)　Write the equilibrium expression for K_s.
  (ii)　Given $K_s = 1.64 \times 10^{-5}$ (mol L^{-1})^3 at SLC, find the $[Ca^{2+}_{(aq)}]$ at equilibrium at SLC.
(HINT: let the $[Ca^{2+}_{(aq)}] = x$ mol L^{-1} thus the $[OH^-_{(aq)}] = 2x$ mol L^{-1})

($[Ca^{2+}_{(aq)}] = 0.0160$ mol L^{-1})

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Q20. At 1000°C the equilibrium constant for:
$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \text{ is } K_c = 174 \text{ L mol}^{-1}.$$
(i) Calculate the concentration of oxygen needed at 1000°C to obtain a 50% conversion of SO_2 into SO_3. (This means that at equilibrium $[SO_3]/[SO_2] = 1.00$)

($[O_{2(g)}] = 0.00575$ mol L^{-1})

(ii) Calculate the concentration of oxygen needed at 1000°C to obtain a 90% conversion of SO_2 into SO_3. (This means that at equilibrium $[SO_3]/[SO_2] = 9.00$)

($[O_{2(g)}] = 0.466$ mol L^{-1})

(iii) Are the answers to parts (i) and (ii) consistent with LCP? Explain.　　　**(yes)**

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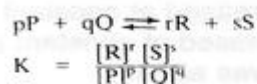　　　　　　　　　　　　　　　　　　　　　　　　　©JAK

EQUILIBRIUM THEORY SUMMARY

- Chemical equilibrium in a closed system at a constant temperature is characterised by the following.
  1 Constant macroscopic properties, including constant concentrations of reactants and products.
  2 Equal reaction rates for the forward and reverse reactions.
- Chemical equilibrium is a dynamic process.
- Equilibrium exists in physical systems, including the following.
  1 Equilibrium between liquid and vapour in a closed system, for example.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

  2 Equilibrium between undissolved solid and dissolved solute in a saturated solution, for example,

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

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

- The equilibrium constant (K) is a number which indicates the relationship between reactant and product concentrations at equilibrium. For the reaction

$$pP + qQ \rightleftharpoons rR + sS$$

$$K = \frac{[R]^r [S]^s}{[P]^p [Q]^q}$$

- The equilibrium constant has the following characteristics.
  1 It is a constant for a reaction at a given temperature.
  2 It does not include terms for substances which occur as solids or liquids in the equation.
- The value of K indicates the relative proportions of reactants and products at equilibrium.
  1 If K is large the reaction favours the formation of products.
  2 If K is small the reaction favours the formation of reactants.
- All reactions are theoretically reversible but:
  1 If K is very large, the reaction will virtually go to completion.
  2 If K is very small, the reaction will not go to any appreciable extent.
- The reaction quotient (Q) includes the same concentration terms as the equilibrium constant but can be used for concentrations other than equilibrium concentrations.
- The value of Q indicates the direction in which a reacting system will move to establish equilibrium.
  1 If Q<K the forward reaction is favoured.
  2 If Q>K the reverse reaction is favoured.
  3 If Q = K the system is at equilibrium.
- Le Chatelier's principle is used to predict the effect of various changes on equilibrium systems. It states that if a chemical system at equilibrium is subjected to a change in conditions, the system will adjust to re-establish equilibrium in such a way as to partially counteract the imposed change.
- Le Chatelier's principle enables the following predictions to be made about the effect of various changes to equilibrium systems.

Change	Direction favoured
increase the concentration of one of the substances	decrease the concentration of that substance
decrease the concentration of one of the substances	increase the concentration of that substance
increase the volume of a gaseous system	increase the number of gaseous molecules
decrease the volume of a gaseous system	decrease the number of gaseous molecules
increase the temperature	endothermic reaction
decrease the temperature	exothermic reaction
add a catalyst	neither

- Industrial chemical processes seek to achieve the maximum yield of product for the minimum cost. Factors affecting reaction rates, equilibrium and economics have to be considered in planning chemical plants. Because factors affecting reaction rates and equilibrium are sometimes in conflict, a compromise set of conditions may be needed in which a reasonable yield is obtained at a satisfactory rate.
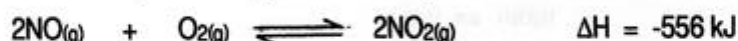
CHEMISTRY
CRITERION 8: EQUILIBRIUM
TEST 5

(Total = 40 marks)

Q1. Consider the equilibrium system involving the oxidation of nitric oxide.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H = -556 \, kJ$$

(a) Which reaction, forward or reverse, favours the attainment of:

      (i) minimum enthalpy? ....

      (ii) maximum entropy? ....
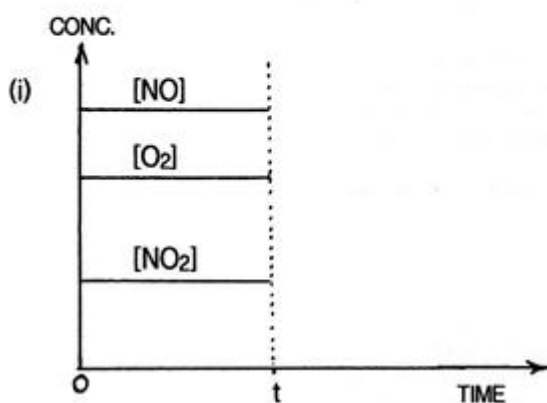
(4 marks)

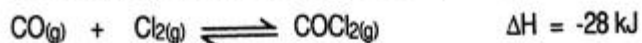(b) What would be the effect on the position of equilibrium if:

      (i) the total pressure was increased at constant temperature?

      (ii) the temperature was increased at constant pressure?

      (iii) an appropriate catalyst was added?

      (iv) the partial pressure of $NO_{(g)}$ was increased?

For each of your answers (i) to (iv), give the appropriate graphical sketch of concentration versus time. Assume the change is imposed at time "t".

(5 marks each)

30   ©JAK

Q2. Consider the equilibrium system as represented by the equation below.

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)} \qquad \Delta H = -28 \text{ kJ}$$

Initially, 5.00 mol of $CO_{(g)}$ and 3.00 mol of $Cl_{2(g)}$ are introduced into a 10.0L container at 450°C. When equilibrium has been established it is found that there is 1.50 mol of carbonyl chloride $COCl_{2(g)}$ present.

(a) Find the mol and hence the **concentration** of each component present at equilibrium. (Hint: use an "ICE" diagram above)

(6 marks)

(b) Find the value for K_c (at 450°C) for the equation as written.

(4 marks)

(c) In an another equilibrium mixture at 450°C it is found that the concentrations of two of the components are:

$$[COCl_{2(g)}] = 0.380 \text{ mol L}^{-1} \text{ and } [Cl_{2(g)}] = 0.410 \text{ mol L}^{-1}$$

Find the concentration of $CO_{(g)}$ in this equilibrium mixture.
(If you were unable to calculate K_c in part (b) use the ficticious value $K_c = 5.00$)

(4 marks)

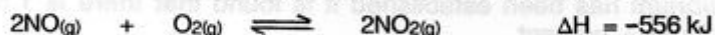(d) Would the value of K_c at 500°C be greater or less than the value at 450°C? Explain briefly.

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TEST ANSWERS

CHEMISTRY
CRITERION. 8: EQUILIBRIUM
TEST 5

(Total = 40 marks)

Q4. Consider the equilibrium system involving the oxidation of nitric oxide.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H = -556\,kJ$$

(a) Which reaction, forward or reverse, favours the attainment of:

    (i) minimum enthalpy? .....FORWARD.....

    (ii) maximum entropy? .....REVERSE.....

(4 marks)

(b) What would be the effect on the position of equilibrium if:

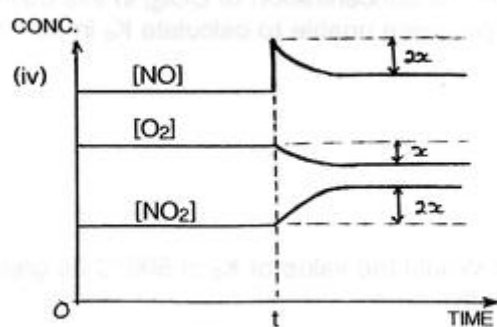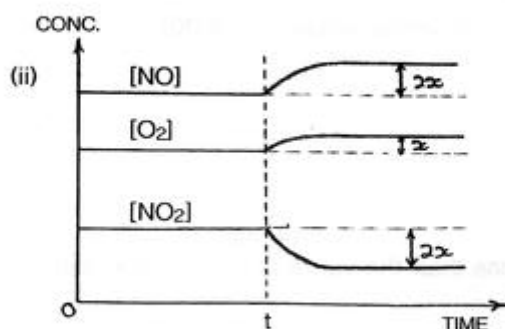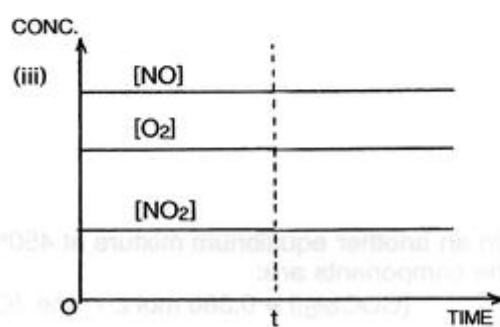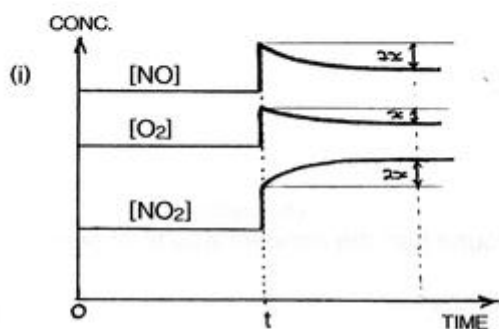   (i) the total pressure was increased at constant temperature?
    (ii) the temperature was increased at constant pressure?
    (iii) an appropriate catalyst was added?
    (iv) the partial pressure of $NO_{(g)}$ was increased?

For each of your answers (i) to (iv), give the appropriate graphical sketch of concentration versus time. Assume the change is imposed at time "t".

(4 marks each)

Q2. Consider the equilibrium system as represented by the equation below.

n	$CO_{(g)}$ +	$Cl_{2(g)}$	$\rightleftharpoons$ $COCl_{2(g)}$
INL	5·00	3·00	—
CHG.	−1·50	−1·50	+1·50
EQM.	3·50	1·50	1·50

$\Delta H = -28\ kJ$

$V = 10·0L$

Initially, 5.00 mol of $CO_{(g)}$ and 3.00 mol of $Cl_{2(g)}$ are introduced into a 10.0L container at 450°C. When equilibrium has been established it is found that there is 1.50 mol of carbonyl chloride $COCl_{2(g)}$ present.

(a) Find the mol and hence the **concentration** of each component present at equilibrium. (Hint: use an "ICE" diagram above)

$$Molarity = \frac{mole}{L}$$

$$\therefore [CO] = \frac{3·50}{10} = 0·350\ mol\ L^{-1}$$

$$[Cl_2] = \frac{1·50}{10} = 0·150\ mol\ L^{-1}$$

$$[COCl_2] = \frac{1·50}{10} = 0·150\ mol\ L^{-1}$$

(6 marks)

(b) Find the value for K_c (at 450°C) for the equation as written.

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0·150}{0·350 \times 0·150}$$

$$= 2·86\ (at\ 450°C)$$

(4 marks)

(c) In an another equilibrium mixture at 450°C it is found that the concentrations of two of the components are:

$$[COCl_{2(g)}] = 0.380\ mol\ L^{-1}\ and\ [Cl_{2(g)}] = 0.410\ mol\ L^{-1}$$

Find the concentration of $CO_{(g)}$ in this equilibrium mixture.
(If you were unable to calculate K_c in part (b) use the ficticious value $K_c = 5.00$)

As it is at 450°C, $K_c = 2·86$

i.e. $\frac{[COCl_2]}{[CO][Cl_2]} = \frac{0·380}{[CO] \times 0·410} = 2·86$

i.e. $[CO] = \frac{0·380}{2·86 \times 0·410}$

$\therefore [CO_{(g)}] = 0·324\ mol\ L^{-1}$

(4 marks)

(d) Would the value of K_c at 500°C be greater or less than the value at 450°C? Explain briefly.

Apply Le Chatelier's Principle:

Inc. temp ∴ system favours endothermic (reverse) reaction

i.e $[COCl_2]$ decreases & $[CO]$ & $[Cl_2]$ increase

(2 marks)

$\therefore K_c = \frac{[COCl_2]}{[CO][Cl_2]}$ will DECREASE !