PART FOUR
CHEMICAL EQUILIBRIUM

Chapter 13
EQUILIBRIUM LAW

INTRODUCTION TO CHEMICAL EQUILIBRIUM

Chemical equilibrium deals with to what extent a chemical reaction proceeds. It is observed that, in most of the chemical reactions, the reactants are not completely converted to products. The reaction proceeds to certain extent and reaches a state at which the concentration of both reactants and product remain constant with time. This state is generally referred to as **equilibrium state**.

- In these reactions, not only the conversion of reactants to products occurs, but also the conversion of products to reactants is possible. The reactions are known as **reversible reactions.**
- Chemical equilibrium deals with these reversible reactions, which reach equilibrium state. The scope of chemical equilibrium includes the study of characteristics and factors affecting the chemical equilibrium.

Reversible and irreversible chemical reactions

Reversible chemical reaction *is the reaction which can proceed in both forward and backward reaction.* A good example of this, is heating of a solid calcium carbonate in the closed vessel.

That is: $CaCO_3(s) \rightleftharpoons CaO(s) + O_2\ (g)$

In the above reaction, the heating must be done in the closed vessel so as to avoid the escape of the carbon dioxide gas from the container otherwise the reaction would be irreversible.

For the reversible reaction, reactants of forward reaction are products of reverse reaction and vice-versa. The symbol $\rightleftharpoons$ is used to indicate that the reaction is reversible.

Irreversible chemical reaction is the reaction which can proceed in one direction only.

A good example of this is heating of potassium chlorate thus decomposing the chlorate into potassium chloride and oxygen gas.

That is: $2KClO_3\ (s) \longrightarrow 2KCl\ (s) + 3O_2\ (g)$

In irreversible reaction, products of forward reaction at given conditions are incapable of reacting in reverse or backward reaction at the same conditions.

So it is clearly understood that, **while in the irreversible system, the reaction may reach to completion, in reversible system the reaction can never reach to completion.**

Chemical equilibrium

Chemical equilibrium *is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction.*

If A reacts with B to form C and D so that they attain chemical equilibrium according to the following equation: $A + B \longrightarrow C + D$

Initially the rate forward reaction is at maximum while that of backward reaction is zero as the only reagents present is A and B while there is no C and D at the beginning of the reaction and hence there is forward reaction only. As the reaction proceed concentration of A and B start to decrease thus lowering the rate of forward reaction while C and D start to be formed leading to backward reaction between C and D to form A and B again. But since concentration of A and B are still high forward reaction is more favoured at initial stages of the reaction. So as the traction proceed the rate of forward reaction is continuously decreasing while that of backward reaction is continuously increasing until the rate of forward reaction is equal to that of backward reaction where it is said that the equilibrium has been attained. This can be verified graphically as follows:

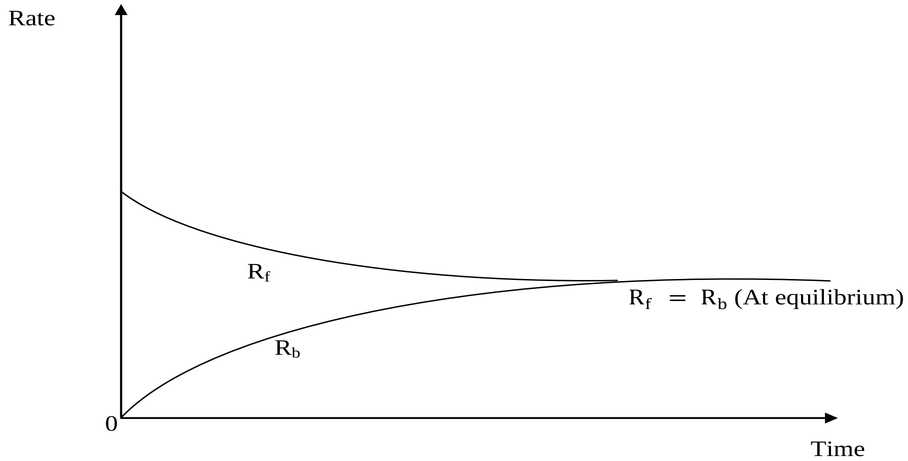


Figure 13.1 Graphical representation of formation of chemical equilibrium

Where:

R_f is the rate of forward reaction.

R_b is the rate of backward reaction

When the equilibrium has been attained the concentrations of reagents involved in the system remain unchanged. In our example, the concentration of A and B is minimum at equilibrium while that of C and D is maximum.

The reader should note that: Chemical equilibrium is also known as **dynamic equilibrium** because it involves balance of the rate of the two reactions (forward and backward reaction) which are proceeding at the same time in opposite directions, that is, **it is an equilibrium involving the constant interchange of particles in motion in opposite directions of forward and reverse reaction.**

Conditions which favour the formation of chemical equilibrium are:

- The system (reaction) must be reversible.
- The reaction should take place in a closed system, that is; no material is allowed to enter or to leave the system.

Homogeneous and heterogeneous chemical equilibrium

Homogeneous chemical equilibrium *is the system of chemical equilibrium where by all reagents involved in the system are in the same phase.*

A good example of this is the reaction between hydrogen and nitrogen gas to form ammonia gas according to the following equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The above reactions are homogeneous chemical equilibrium because all reagents (N_2, H_2 and $2NH_3$) are in the same gaseous phase.

Heterogeneous chemical equilibrium *is the system of chemical equilibrium where by reagents involved in the system are in different phase.*

A good example of this is the decomposition of solid ammonium chloride to form ammonia gas and hydrogen chloride gas.

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

Another example is the heating of solid calcium carbonate to form a solid calcium oxide and carbon dioxide gas.

$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

Characteristics of chemical equilibrium

1) At equilibrium state, the rates of forward and backward reactions are equal.
2) The observable properties such as pressure, concentration, colour, density, viscosity etc., of the system remain unchanged with time once the system has attained chemical equilibrium.
3) The chemical equilibrium is a **dynamic equilibrium** because both the forward and backward reactions continue to occur even through it appears static externally.
   In other words: the concentration of reactions and products do not change with time but their inter – conversion continue to occur.
4) The chemical equilibrium can be reached by starting the reaction either from the reactants side or from the product side.
5) Both pressure and concentration affect the position of equilibrium but do not affect the equilibrium constant (the concept of **equilibrium constant** will be discussed in the later).
6) The temperature can affect both the position of equilibrium as well as the equilibrium constant.
7) A positive catalyst can increase the rates of both forward and backward reactions and thus helping the system to attain the equilibrium faster. But it does not affect the position of equilibrium and equilibrium constant.

EQUILIBRIUM LAW

We have seen that when the reversible reaction is allowed to attain equilibrium, the concentration of reactants and products remains unchanged. Equilibrium law help us to understand these equilibrium concentrations better. It states that: *When a chemical system is allowed to reach the equilibrium at a particular temperature, there is a fixed ratio of product of concentration of products to that of reactants raised to powers equals to stoichiometric coefficients regardless to the original concentration of the reagents present in the system.*

The equilibrium law is also known as the **law of mass action** because in the early days of chemistry *concentration* was called *'active mass'*.

However strictly speaking, equilibrium law is just a special case of law of mass action. The more general form of law of mass action may be stated as: *The rate of reaction at an instant of time is proportional to the product of active masses of reactants at that instant of time under given conditions.* This law is the basis of derivation of equilibrium stated above.

The active masses for different substances and systems can be expressed as mentioned below.

1) For dilute solution, the molar concentrations are taken as active masses.
2) For gases at low pressure, the partial pressures are taken as active masses. However, the molar concentration can also be taken as active masses.
3) The active masses of pure solids and pure liquids are taken as unity (1) since their active masses (or concentration) are independent of their quantities taken.

Equilibrium constant

The equilibrium law has introduced an idea of having fixed ratio of equilibrium concentrations. The fixed ratio is known as **equilibrium constant**. It can be defined as *the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients*.

Thus the equilibrium constant is the fixed ratio which is obtained according to the law of mass action (equilibrium law)

For the reaction: $\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cC} + \mathrm{dD}$

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

Where: Where K is equilibrium constant

c (subscript in K) insists that the equilibrium constant is in terms of concentration.

$\frac{[C]^c[D]^d}{[A]^a[B]^b}$ is equilibrium constant expression

And the whole equation $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ is known as equilibrium constant equation

[ ] is the molar concentration at equilibrium (equilibrium concentration)

a, b, c and d are stoichiometric coefficients of A, B, C and D respectively

K_c is more commonly given in units of $moldm^{-3}$(M) raised to certain powers; so whenever its units are deliberately omitted in the examination question, you must insert appropriate units in terms of $moldm^{-3}$ in your calculations.

It should be understood that:

The value of equilibrium constant does not depend on the original concentration of the reagents in the system, it is only temperature dependent.

Significance of equilibrium constant

The value of equilibrium constant K_c is important in predicting the extent of forward reaction or backward reaction of which a particular reaction proceeds:

- If K_c is too large then the reaction is more forward (the reaction will reach equilibrium when most of the reactant has been converted to product).
- If K_c is too small then the reaction is more backward (the reaction achieves equilibrium after very little reactant has been converted to product).

We can make the following generalisation concerning the composition of equilibrium mixtures:

- If $K_c > 10^3$, products predominate over reactants.
- \- If K_c is very large (approaches infinity), the reaction proceeds nearly to completion.
- If $K_c < 10^{-3}$, reactants predominate over products.
- \- If K_c very small (approach zero), there is almost no reaction
- If $10^{-3} \leq K_c \leq 10^3$, appreciable concentration of both reactants and products are present.

Keep in mind that the magnitude of equilibrium constant (K_c) does not indicate how rapidly or slowly equilibrium will be reached.

Worked examples

Example 1

When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?

(a) $H_2(g) + S(s) \rightleftharpoons H_2S$; $K_c = 7.8 \times 10^5$

(b) $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$; $K_c = 7.4 \times 10^{-26}$

Solution

(a) Contain mostly products ($K_c > 10^3$)

(b) Contain mostly reactants ($K_c < 10^{-3}$)

Example 2

Which of the following reactions yield appreciable equilibrium concentration of both reactants and products?

(a) $2Cu(s) + O_2(g) \rightleftharpoons 2CuO(s)$; $K_c = 4 \times 10^{45}$

(b) $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$; $K_c = 7.5 \times 10^{-3}$

(c) $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$; $K_c = 2 \times 10^{-19}$

Solution

(b) Its K_c value is between of $10^{-3}$and 10^3

Example 3

When wine spoils, ethanol is oxidised to acetic acid as O_2 from the air reacts with the wine;

$$\underset{\text{Ethanol}}{CH_3CH_2OH(aq)} + O_2(aq) \rightleftharpoons \underset{\text{acetic acid}}{CH_3CO_2H(aq)} + H_2O(l)$$

The value of K_c for this reaction at 25°C is 1.2×10^{82}. Will much ethanol remain when the reaction has reached equilibrium? Explain.

Solution

No. There is almost no ethanol at all when the reaction is at equilibrium.

Explanation

K_c for the reaction very large suggesting that the reaction reach almost to completion. So ethanol being at reactant side will almost be completely consumed when the reaction has reached equilibrium.

Homogeneous and heterogeneous equilibrium constants

Equilibrium constant obtained in homogeneous chemical equilibrium is known as **homogeneous equilibrium constant** while equilibrium constant obtained in heterogeneous chemical equilibrium is known as **heterogeneous equilibrium constant.**

For homogeneous chemical equilibrium, the equilibrium constant expression involves all reagents involved in the system while for heterogeneous equilibrium constant the following order of preference must be considered in selecting terms which should appear in the equilibrium constant expression.

Gas > Solution > Liquid > Solid

As a general rule, **the concentration of pure solids and pure liquids are not included when writing equilibrium constant equation**.

We include only the concentrations of gases and the concentrations of solute in solutions because only those concentrations can be varied. Concentrations of pure solids and liquids depend only on their densities which are independent of their quantities taken and hence they are taken as unity (1) or constant.

Worked examples in writing equilibrium constant expression

Example 4

Writing an expression for equilibrium constant (K_c) for the reaction,

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

(i) A, B, C and D are gases.
(ii) A, B, C and D are solutions
(iii) A and C are solid while B and D are gases.
(iv) C is solid and A, B and D are solutions.

Solution

(i) $K_c = \frac{[C][D]}{[A][B]}$

This is the homogeneous equilibrium constant, so all terms must appear in the equilibrium constant expression.

(ii) $K_c = \frac{[C][D]}{[A][B]}$

This is also homogeneous equilibrium constant, so all terms must appear in the equilibrium constant expression.

(iii) $K_c = \frac{[D]}{[B]}$

This is the heterogeneous equilibrium constant, so as gaseous phase dominates solid phase in the order of selection of terms, A and C which are solids are do not appear in the expression.

(iv) $K_c = \frac{[D]}{[A][B]}$

This is the heterogeneous equilibrium constant, so as liquid phase (solution) outweighs solid phase in the order of selection of terms, C which is solid does not appear in the

Example 5

Write the equilibrium constant expression (K_c) for each of the following reactions:

(a) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$
(b) $Hg(l) + Hg^{2+}(aq) \rightleftharpoons Hg_2^{2+}(aq)$

Solution

(a) $K_c = \frac{[CO]^2}{[CO_2]}$

Here C(s) is omitted because it is pure solid.

(b) $K_c = \frac{[Hg_2^{2+}]}{[Hg^{2+}]}$

Here Hg (l) is omitted because it is pure liquid.

Example 6

Write the equilibrium constant (K_c) for the following reversible reactions.

(i) $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$
(ii) $C\ (s) + ½\ O_2\ (g) \rightleftharpoons CO\ (g)$
(iii) $C_2H_6\ (g) + \frac{7}{2}O_2\ (g) \rightleftharpoons 3H_2O\ (l) + 2CO_2\ (g)$
(iv) $CaCO_3\ (s) \rightleftharpoons CaO(s) + CO_2(g)$
(v) $NH_4HS\ (s) \rightleftharpoons NH_3(g) + H_2S\ (g)$

Solution

(i) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$
(ii) $K_c = \frac{[CO]}{[O_2]^{1/2}}$
(iii) $K_c = \frac{[CO_2]^2}{[C_2H_6][O_2]^{7/2}}$
(iv) $K_c = [co_2]$
(v) $K_c = [NH_3][H_2S]$

Example 7

Write the chemical equation that has the following homogeneous equilibrium constant expression;
$K_c = \frac{[CO]^2[O_2]}{[CO_2]^2}$

Solution

Reagent on the numerator of K_c expression appears as product in the equation while reagents in the denominator of the expression appear as reactant. That is $CO_2 \rightleftharpoons CO + O_2$
Powers in the concentration of each reagent are stoichiometric coefficients of the respective reagents in the equation: That is $2CO_2 \rightleftharpoons 2CO + O_2$
Hence the chemical equation corresponding to the given equilibrium constant expression is;

$$2CO_2 \rightleftharpoons 2CO + O_2$$

Example 8

Given that: $A + B \rightleftharpoons C$; $K_c = 10dm^3mol^{-1}$ at $25°C$

Find the equilibrium constant, K_c, for the following reaction at $25°C$;

$$C \rightleftharpoons A + B$$

Solution

With the equation, $C \rightleftharpoons A + B$

$$K_c = \frac{[A][B]}{[C]} = \frac{1}{\frac{[C]}{[A][B]}}$$

But $\frac{[C]}{[A][B]} = K_c$ for $A + B \rightleftharpoons C$ which is $10dm^3mol^{-1}$

It follows that; $K_c = \frac{1}{10dm^3mol^{-1}} = 0.1moldm^{-3}$

Hence the K_c value for the given reaction is $0.1moldm^{-3}$

The reader should notice that:

In the above example, the second equation, $C \rightleftharpoons A + B$, is the reverse of the first equation $(A + B \rightleftharpoons C)$ and therefore the result obtained can be generalised into the following rule;

If the equation is reversed, the equilibrium constant is reciprocated.

Example 9

Given that: $A + B \rightleftharpoons C + D$; $K_c = 10$ at $25°C$

Find the equilibrium constant, K_c for the following reaction at $25°C$; $2A + 2B \rightleftharpoons 2C + 2D$

Solution

With equation, $2A + 2B \rightleftharpoons 2C + 2D$

$$K_c = \frac{[C]^2[D]^2}{[A]^2[B]^2} = \left(\frac{[C][D]}{[A][D]}\right)^2$$

But $\frac{[C][D]}{[A][D]} = K_c$ for $A + B \rightleftharpoons C + D$ which is 10

It follows that; $K_c = 10^2 = 100$

Hence the K_c value for the given reaction is 100

Again, you should notice that:

In this example, the second equation$(2A + 2B \rightleftharpoons 2C + 2D)$ can be obtained by multiplying the first equation $(A + B \rightleftharpoons C + D)$ by 2. So the obtained result can also be generalised to the following rule:

If the equation is multiplied by a factor, the equilibrium constant is raised to the same factor.

Example 10

Given that: $A + B \rightleftharpoons C$; $K_c = 10dm^3mol^{-1}$

$P + Q \rightleftharpoons R + S + T$; $K_c = 100moldm^{-3}$

Find the equilibrium constant, K_c, for the following reaction:

$$A + B + P + Q \rightleftharpoons +C + R + S + T$$

Solution

With the equation, $A + B + P + Q \rightleftharpoons +C + R + S + T$

$$K_c = \frac{[C][R][S][T]}{[A][B][P][Q]} = \left(\frac{[C]}{[A][B]}\right)\left(\frac{[R][S][T]}{[P][Q]}\right)$$

But $\frac{[C]}{[A][B]} = K_c$ for $A + B \rightleftharpoons C$ which is $10dm^3\ mol^{-1}$

And $\frac{[R][S][T]}{[P][Q]} = K_c$ for $P + Q \rightleftharpoons R + S + T$ which is $100moldm^{-3}$

It follows that; $K_c = 10dm^3mol^{-1} \times 100moldm^{-3} = 1000$

Hence the K_c for the given reaction is 1000

Here there is a final thing to notice!

In this example, the third equation $(A + B + P + Q \rightleftharpoons +C + R + S + T)$ is the sum of other first two equations$(A + B \rightleftharpoons C$ and $P + Q \rightleftharpoons C + R + S + T)$.

So the obtained result can also be generalised to the following rule:

When chemical equations are added, their equilibrium constants are multiplied together to get the overall equilibrium constant.

Putting all three rules together!

The previous last three examples gave us the **rules of manipulating equilibrium constant**, which may be assembled together as follows:

Rule 1:

If the equation is reversed, the equilibrium constant is reciprocated.

Rule2:

If the equation is multiplied by a factor, the equilibrium constant is raised to the same factor.

Rule 3:

When chemical equations are added, their equilibrium constants are multiplied together to get the overall equilibrium constant.

Example 11

Given the following information:

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq);\ K_c = 6.8 \times 10^{-4}$

$H_2C_2O_4(aq) \rightleftharpoons 2H^+(aq) + C_2O_4^{2-}(aq);\quad K_c = 3.8 \times 10^{-6}$

Determine the value of K_c for the reverse reaction?

$2HF(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2F^-(aq) + H_2C_2O_4(aq)$

Solution

Given that

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)K_{C_1} = 6.8 \times 10^{-4} \dots\dots\dots\dots\dots\dots\dots\dots.(i)$

$H_2C_2O_4(aq) \rightleftharpoons 2H^+(aq) + C_2O_4^{2-}(aq)K_{C_2} = 3.8 \times 10^{-6} \dots\dots\dots..(ii)$

Taking 2(i) gives;

$2HF(aq) \rightleftharpoons 2H^+(aq) + 2F^-(aq); K_{C_3} = \left(K_{C_1}\right)^2 \dots\dots\dots\dots..\dots\dots..(iii)$

Revering (ii) gives;

$2H^+(aq) + C_2O_4^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq);\ K_{C_4} = \frac{1}{K_{C_2}} \dots\dots\dots\dots\dots\dots.\dots\dots(iv)$

Taking (iii) + (iv) gives;

$2HF(aq) + 2H^+(aq) + C_2O_4^{2-} \rightleftharpoons 2H^+(aq) + 2F^-(aq) + H_2C_2O_4(aq)$

Or $2HF(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2F^-(aq) + H_2C_2O_4(aq);\ K_C = K_{C_3} \times K_{C_4}$

Thus the required $Kc = \left(K_{C_1}\right)^2 \times \frac{1}{K_{C_2}} = (6.8 \times 10^{-4})^2 \times \frac{1}{3.8\times10^{-6}} = 0.1217$

Hence the K_c of the given reaction is 0.1217

Relationship between equilibrium constant and rate constants

Equilibrium constant, K_c relate to rate constants of forward and backward reaction according to the following equation: $K_c = \frac{K_f}{K_b}$

Where K_f is the **rate constant (or velocity constant)** of forward reaction

And K_b (or K_r)is the **rate constant (velocity constant)** of backward (or reverse) reaction.

To understand this considers the following **single bimolecular step** reversible chemical reaction:

$A + B \rightleftharpoons C + D$

From which: $R_f = K_f [A] [B]$

$R_b = K_b [C] [D]$

Where R_f and R_b are rates of forward and backward reaction respectively

But at equilibrium; $R_f = R_b$

Then $K_f [A] [B] = K_b [C] [D]$

From which: $\frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$

But $\frac{[C][D]}{[A][B]} = K_c$

Hence $\mathbf{K_c} = \frac{\mathbf{K_f}}{\mathbf{K_b}}$

Understand this!

Deriving above relationship by using by more general equation; $aA + bB \rightleftharpoons cC + dD$, is beyond the scope of this book. As we know, the rate law of multistep reaction **cannot** be deduced from balanced chemical equation by simply writing $R_f = K_f[A]^a[B]^b$ or $R_b = K_b[C]^c[D]^d$. That is **not** correct; we can only deduce rate law directly from chemical equation if the reaction follows **single step** mechanism as we have learned in the chemical kinetics.

Calculations involving equilibrium constant

Example 12

Alcohol reacts in reversible reaction with acid to form ester and water:

i.e. $\text{Alcohol} + \text{Acid} \rightleftharpoons \text{Ester} + \text{water}$

When 1 mole of ethanol (ethyl alcohol) reacts with 1 mole ethanoic acid until equilibrium at certain temperature, 0.333 mole of each alcohol and acid and 0.666 mole of each ester and water will be present; calculate the amount of ester when:

(a) 3 moles of ethanol are mixed with 1 mole of ethanoic acid
(b) 92g of ethanol ($\text{r.m.m} = 46$) are mixed with 60g of ethanol acid ($\text{r.m.m} = 60$)
(c) 1 mole of ethanol is mixed with 1 mole of acid in presence of 1 mole of water.

Solution

$$K_c = \frac{[\text{Ester}][\text{Water}]}{[\text{Alcohol}][\text{Acid}]}$$

Where $[\quad] = \frac{n}{V}$

$$K_c = \frac{\left(\frac{0.666}{V}\right)\left(\frac{0.666}{V}\right)}{\left(\frac{0.333}{V}\right)\left(\frac{0.333}{V}\right)} = \frac{(0.666)^2}{(0.333)^2} = 4$$

(a)

	Alcohol +	Acid	$\rightleftharpoons$	Ester +	Water
Initially	3	1		0	0
At equilibrium	$3 - x$	$1 - x$		x	x

$$K_c = \frac{\frac{x}{V} \times \frac{x}{V}}{\left(\frac{3-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 4x + 3}$$

Since K_c does not depend on original amount of reagents present in the system then;

$$4 = \frac{x^2}{x^2 - 4x + 3};$$

$$4x^2 - 16x + 12 = x^2;$$

$$3x^2 - 16x + 12 = 0$$

$x = 0.9$ ($x = 4.43$ is not practical answer because it exceeds the initial amount of alcohol and acid)

Hence the amount of ester is 0.9moles.

(b) Using $n = \frac{m}{M_r}$

Number of moles of ethanol = $\frac{92\text{g}}{46\text{gmol}^{-1}} = 2\text{mol}$

Number of moles of ethanoic acid = $\frac{60\text{g}}{60\text{gmol}^{-1}} = 1\text{mol}$

	Alcohol +	Acid	$\rightleftharpoons$	Ester +	Water
Initially	2	1		0	0
At equilibrium	$2 - x$	$1 - x$		x	x

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 3x + 2} = 4$$

Then: $3x^2 - 12x + 8 = 0$; $x = 0.8$

Amount of ester present at equilibrium is 0.8moles.

(c)

	Alcohol +	Acid	⇌	Ester	+ Water
Initially	1	1		0	1
At equilibrium	$1-x$	$1-x$		x	$1+x$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{1+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2+x}{x^2-2x+1} = 4$$

Then; $4x^2 - 8x + 4 = x^2 + x$

Or $3x^2 - 9x + 4 = 0; x = 0.54$

Hence the amount of ester is 0.54moles.

Example 13

1 mole of dinitrogen tetraoxide was allowed to dissociate to nitrogen dioxide gas in a flask of certain volume at 500K. At equilibrium 1 mole of nitrogen dioxide was found to be present. If the equilibrium constant for the reaction is 0.4molL^{-1}. Calculate the volume of the flask.

Solution

The reaction equation;

	$N_2O_4(g)$	⇌	$2NO_2(g)$
Initially	1		0
At equilibrium	$1-x$		2x

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)} = \frac{4x^2}{(1-x)V}$$

But at equilibrium 1mole of nitrogen dioxide was found to be present;

So $2x = 1$ or $x = 0.5$

Then;

$$K_c = 0.4\text{molL}^{-1} = \frac{4 \times 0.5^2\text{mol}^2}{V(1-0.5)\text{mol}}$$

From which; $V = 5\text{L}$

The volume of the flask is 5L

Example 14

The value of K_c for the reaction:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ at 750°C is 0.771. If 1 mole of hydrogen gas and 1 mole of carbon dioxide are mixed in 1 Litre container at 750°C; what are concentrations of all substances at equilibrium?

Solution

	$H_2(g)$	+ $CO_2(g)$	⇌	$H_2O(g)$	+ $CO(g)$
Initially	1	1		0	0
At equilibrium	$1-x$	$1-x$		x	x

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 2x + 1} = 0.771$$

Then $0.229x^2 + 1.54x - 0.771 = 0$

$x = 0.4675$

Using $[\quad] = \frac{n}{V}$

$[H_2O] = \frac{0.4675}{1} M = 0.4675M$

$[CO] = \frac{0.4675}{1} M = 0.4675M$

$[H_2] = \frac{(1-0.4675)}{1} M = 0.5325M$

$[CO_2] = \frac{(1-0.4675)}{1} M = 0.5325M$

Example 15

12g of acetic acid is heated with 18.6g of ethanol in $1dm^3$ flask at 298K. At equilibrium the amount of acetic acid which remains unreacted was found to be 1.8g. Calculate the equilibrium constant.

Solution

Initially: Number of moles of acetic acid = $\frac{12g}{60gmol^{-1}} = 0.2mol$

Number of moles ethanol = $\frac{18.6g}{46gmol^{-1}} = 0.4mol$

At equilibrium: Number of moles acetic acid = $\frac{1.8g}{60gmol^{-1}} = 0.03mol$

	$CH_3COOH\ (l)\ +$	$C_2H_5OH\ (l)$	$\rightleftharpoons$	$CH_3COOC_2H_5\ (l)\ +$	$H_2O(l)$
Initially	0.2	0.4		0	0
At equilibrium	$0.2 - x$	$0.4 - x$		x	x

$$K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.2-x}{V}\right)\left(\frac{0.4-x}{V}\right)} = \frac{x^2}{x^2 - 0.6x + 0.08}$$

But at equilibrium, number of moles of CH_3COOH is 0.03mol

Then $0.2 - x = 0.03$ or $x = 0.17$

Then $K_c = \frac{0.17^2}{0.17^2 - (0.6 \times 0.17) + 0.08} = 4.1884$

Thus the equilibrium constant is 4.1884

Example 16

1 mole of hydrogen gas and 1 mole of iodine are mixed together in $1dm^3$ flask and the reaction was allowed to establish the equilibrium at 473K. Calculate the percentage of HI if the equilibrium constant is 4.

Solution

	$H_2\ (g)\ +$	$I_2\ (g)$	$\rightleftharpoons$	$2HI\ (g)$
Initially	1	1		0
At equilibrium	$1 - x$	$1 - x$		$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{4x^2}{x^2 - 2x + 1} = 4$$

Then: $4x^2 = 4x^2 - 8x + 4$

From which; $8x = 4$ or $x = 0.5$

At equilibrium; $n_T = 1 - x + 1 - x + 2x = 2$ and $n_{HI} = 2x = 2 \times 0.5 = 1$

Then $\%HI = \frac{n_{HI}}{n_T} \times 100\% = \frac{1}{2} \times 100\% = 50\%$

Hence the percentage of HI is 50%

Example 17

$6.22cm^3$ of the gas G_2 was mixed with $5.6\ cm^3$ of the L_2 gas in $1dm^3$ flask at 25°C. At equilibrium $9.66cm^3$ of GL were found in the flask. Calculate the equilibrium constant.

The reaction equation is $G_2\ (g) + L_2\ (g) \rightleftharpoons 2GL\ (g)$

Solution

For gases: Mole ratio = volume ratio (This fact is derived from Avogadro's law)

Then the volume of each gas at equilibrium can be deduced as follows:

	$G_2\ (g)$	$+\ L_2\ (g)$	$\rightleftharpoons 2GL\ (g)$
Initially:	6.22	5.6	0
At equilibrium:	$6.22 - x$	$5.6 - x$	$2x$

Then $K_c = \frac{[GL]^2}{[G_2][L_2]} = \frac{\left(\frac{n_{GL}}{V}\right)^2}{\left(\frac{n_{G_2}}{V}\right)\left(\frac{n_{L_2}}{V}\right)}$ where V is the volume of the flask

Then $K_c = \frac{(n_{GL})^2}{n_{G_2} \times n_{L_2}} = \frac{n_{GL}}{n_{G_2}} \times \frac{n_{GL}}{n_{L_2}}$

But $\frac{n_{GL}}{n_{G_2}} = \frac{V_{GL}}{V_{G_2}}$ and $\frac{n_{GL}}{n_{L_2}} = \frac{V_{GL}}{V_{L_2}}$ (From Avogadro's law)

Thus $K_c = \frac{V_{GL}}{V_{G_2}} \times \frac{V_{GL}}{V_{L_2}} = \frac{(2x)^2}{(6.22-x)(5.6-x)} = \frac{4x^2}{(6.22-x)(5.6-x)}$

But at equilibrium, $9.66\ cm^3$ of GL were found to be present in the flask.

Thus; $2x = 9.66$ or $x = 4.83$

Then $K_c = \frac{4 \times 4.83^2}{(6.22-4.83)(5.6-4.83)} = 87.2$

Hence the equilibrium constant is 87.2

Example 18

At certain temperature, $K_c = 4$ for the following reaction:

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g)$$

The maximum amount of $F_2(g)$ that was formed in the course of the above reaction in a 1.0L closed reaction vessel was found to be 0.045mol. What was initial amount of HF in the reaction vessel? (Assume initially there were HF only in the vessel).

Solution

The maximum amount of $F_2(g)$ is formed when the reaction is at equilibrium. Thus 0.045mol is an equilibrium amount of $F_2(g)$.

Reaction equation;

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g)$$

Initial number of moles	h	0	0
Number of moles at equilibrium	h − 2x	x	x

Then;

$$K_c = \frac{[H_2][F_2]}{[HF]^2} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{h-x}{V}\right)^2} = \frac{x^2}{(h-2x)^2}$$

Substituting;

$$4 = \frac{(0.045)^2}{(h - 2 \times 0.045)^2}$$

Then;

$$\sqrt{4} = \sqrt{\frac{(0.045)^2}{(h - 2 \times 0.045)^2}};\ 2 = \frac{0.045}{h - 0.09}$$

From which; $h = 0.1125\text{mol}$

The initial amount of HF was 0.1125mol

Equilibrium constant in terms of partial pressures, K_p

Partial pressure of gas varies direct proportional to its molar concentration (concentration in mol/dm^3); this can be clearly understood by considering the ideal gas equation which is;

$PV = nRT$.

From which: $P = \left(\frac{n}{V}\right)RT$

But $\frac{n}{V}$ = Molar concentration, [ ]

Thus P = [ ] RT

For given (constant) temperature: RT = Constant

Then P = Constant × [ ]

Hence P ∝ [ ]

So for gases it is possible to write equilibrium constant in terms of partial pressure, that is; for the system of chemical equilibrium whose reagents are in gaseous state, the equilibrium constant (K_P) expression can be written as follows:

If $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

Then $\mathbf{K_p} = \frac{(\mathbf{P_C})^c(\mathbf{P_D})^d}{(\mathbf{P_A})^a(\mathbf{P_B})^b}$

Where $\mathbf{P_A}, \mathbf{P_B}, \mathbf{P_C}$ and $\mathbf{P_D}$ are partial pressures of A, B, C and D respectively.

K_p is more commonly given in units of atm raised to certain powers (rather than Nm^{-2} or mmHg), so whenever its units are deliberately omitted (in the examination question), you should assume the units in terms of atm.

Also it is important to keep in mind that, for gases, equilibrium constant is more commonly given in terms of partial pressures (K_p) than concentrations (K_c). So whenever you are asked about just equilibrium constant without specifying whether it is K_c or K_p and the question is about gaseous equilibrium, the implication is K_p.

Example 19

The reaction of the formation of the nitrosyl chloride;

$2NO\ (g) + Cl_2\ (g) \rightleftharpoons 2NOCl\ (g)$ was studies at 25°C. The partial pressure at equilibrium

Were found to be: $P_{NOCl} = 12atm$

$P_{NO} = 5 \times 10 - 2\ atm$

$P_{Cl_2} = 3 \times 10^{-1}\ atm$

Calculate the value of K_p for the reaction

Solution

$$K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2(P_{Cl_2})} = \frac{(12atm)^2}{(5 \times 10^{-2}atm)^2(3 \times 10^{-1}atm)} = 192000atm^{-1}$$

Thus K_p is 192000atm^{-1}

Example 20

For the reaction: $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

(a) Calculate the mole percentage of ammonia in the equilibrium mixture formed at 400°C and 3×10^7Pa pressure when gaseous hydrogen and nitrogen are mixed in 3:1 mole ratio and there is 61% conversion of nitrogen to ammonia.
(b) Calculate the value of K_p in (a) above.

Solution

For 'a' moles of N_2 there are 3a moles of H_2, i.e. $n_{H_2} : n_{N_2} = 3:1$ (given)

	$N_2\ (g)$ +	$3H_2\ (g)$ $\rightleftharpoons$	$2NH_3\ (g)$
Initially	a	3a	0
At equilibrium	$a - x$	$3a - 3x$	$2x$

At equilibrium: $n_T = (a - x) + (3a - 3x) + 2x = 4a - 2x$

$$\%NH_3 = \frac{n_{NH_3}}{n_T} \times 100\% = \left(\frac{2x}{4a - 2x}\right) \times 100\%$$

But $x = \frac{61a}{100} = 0.61a$

Then % NH_3 = $\frac{2 \times 0.61a}{4a - (2 \times 0.61a)} \times 100\% = \frac{1.22a}{2.78a} \times 100\% = 43.88\%$

(a) Percentage of ammonia is 43. 88%

$$P_{N_2} = X_{N_2}P_T = \left(\frac{a - x}{4a - 2x}\right)P_T$$

$$P_{H_2} = X_{H_2}P_T = \left(\frac{3a - 3x}{4a - 2x}\right)P_T$$

$$P_{NH_3} = X_{NH_3}P_T = \left(\frac{2x}{4a - 2x}\right)P_T$$

Substituting x = 0.61a in each of the above expression for partial pressure:

$$P_{N_2} = \frac{0.39a}{2.78a}P_T = 0.14P_T$$

$P_{H_2} = \frac{1.17a}{2.78a} P_T = 0.42P_T$

$P_{NH_3} = \frac{1.22a}{2.78a} P_T = 0.4388P_T$

$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})} = \frac{(0.4388P_T)^2}{(0.42P_T)^3(0.14P_T)} = \frac{18.56}{{P_T}^2}$

But $P_T = 3 \times 10^7$ Pa

$K_p = \frac{18.56}{(3 \times 10^7 Pa)^2} = 2.062 \times 10^{-14} Pa^{-2}$

(b) Hence K_p is $2.062 \times 10^{-14} Pa^{-2}$

Example 21

1.28 moles of dinitrogen tetraoxide (N_2O_4) was allowed to dissociate into nitrogen dioxide (NO_2) in a 5 litres vessel at 298K. At equilibrium 75% was found to be undissociated and the total pressure was 15 atm. What would be the degree of dissociation of N_2O_4 if the total pressure of the mixture was 10 atm?

Solution

Degree of dissociation is (100 – 75) % = 25%

	N_2O_4 (g) $\rightleftharpoons$	$2NO_2$ (g)
Initially	1.28	0
At equilibrium	$1.28 - x$	2x

Then $K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(X_{NO_2}P_T)^2}{X_{N_2O_4}P_T} = \frac{{X_{NO_2}}^2 P_T}{X_{N_2O_4}}$

But $n_T = (1.28 - x) + 2x = 1.28 + x$

So $X_{NO_2} = \frac{2x}{1.28+x}$

And $X_{N_2O_4} = \frac{1.28-x}{1.28+x}$

Then $K_p = \frac{\left(\frac{2x}{1.28+x}\right)^2 P_T}{\left(\frac{1.28-x}{1.28+x}\right)} = \frac{4x^2P_T}{1.28^2 - x^2}$

Thus $K_p = \frac{4x^2P_T}{1.6384 - x^2}$

But $x = \frac{25}{100} \times 1.28 moles = 0.32 moles$

And $P_T = 15atm$

Therefore: $K_p = \frac{4 \times 0.32^2 \times 15atm}{1.6384 - 0.32^2} = 4atm$

If the total pressure, P_T is changed to 10atm, the value of K_p remains the same (K_p is only temperature dependent like K_c)

Thus $K_p = 4 = \frac{10 \times 4x^2}{1.6384 - x^2}$ Or $40x^2 = 4 \times 1.6384 - 4x^2$

Or $44x^2 = 4 \times 1.6384 = 6.5536$

$x = \sqrt{\frac{6.5536}{44}} = 0.386$

$$\text{Degree of dissociation}, \alpha = \frac{\text{Number of moles dissociated}}{\text{Number of moles before dissociation}} = \frac{0.386}{1.28} = 0.3 \text{ or } 30\%$$

Alternative solution:

Since the equilibrium constant does depend on initial amount of reagents present in the system, for simplifying the work we may assume 1 mole as initial amount of N_2O_4 instead of the given 1.28 moles.

When the initial amount is 1mole, numerical value of number of moles dissociated is equal to the numerical value for the degree of the dissociation, α

	N_2O_4 (g)	⇌	$2NO_2$ (g)
Initially	1		0
At equilibrium	1 – α		2α

$$\text{Then } K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(X_{NO_2}P_T)^2}{X_{N_2O_4}P_T} = \frac{{X_{NO_2}}^2P_T}{X_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 P_T}{\left(\frac{1-\alpha}{1+\alpha}\right)} = \boldsymbol{\frac{4\alpha^2P_T}{1-\alpha^2}}$$

But $\alpha = \frac{25}{100} = 0.25$ and $P_T = 15\text{atm}$

$$\text{Then } K_p = \frac{4 \times 0.25^2 \times 15}{1 - 0.25^2}\text{atm} = 4\text{atm}$$

When $P_T = 10\text{atm}$

$4 = \frac{4\alpha^2P_T}{1-\alpha^2} = \frac{10\times4\alpha^2}{1-\alpha^2} = \frac{40\alpha^2}{1-\alpha^2}$ or $44\alpha^2 = 4$ or $\alpha = 0.3$

Hence the degree of dissociation is 0.3 or 30%.

It can be recognised that the second method is easier one and is more useful when the question is concerned with the degree of dissociation.

Example 22

0.8 moles of PCl_5 was allowed to dissociate to PCl_3 and Cl_2 in $5dm^3$ vessels at 250°C. At equilibrium 60% of PCl_5 was found to dissociate completely and the total pressure was measured to be 30mmHg. Calculate:

(i) Equilibrium constant, K_p

(ii) What would be the total pressure if the degree of dissociation of PCl_5 was 35%?

Solution

Since the equilibrium constant does not depend on the initial amount of reagents present in the system, for simplifying the work we may assume the initial amount to be 1 mole instead of the given 0.8 moles.

Equilibrium for the reaction is:

	$PCl_5(g)$	⇌	$PCl_5(g)$	+	$Cl_2(g)$
Initially	1		0		0
At equilibrium	1 – α		α		α

$n_T = (1 - \alpha) + 2\alpha = 1 + \alpha.$

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{(X_{PCl_3}P_T)(X_{Cl_2}P_T)}{(X_{PCl_5}P_T)} = \frac{\left(\frac{\alpha}{1+\alpha}\right)P_T\left(\frac{\alpha}{1+\alpha}\right)P_T}{\left(\frac{1-\alpha}{1+\alpha}\right)P_T} = \frac{\alpha^2P_T}{1-\alpha^2}$$

(a) When $\alpha = \frac{60}{100} = 0.6$

$$K_p = \frac{0.6^2 \times 30\text{mmHg}}{1 - 0.6^2} = 16.875\text{mmHg}$$

(b) When $\alpha = \frac{35}{100} = 0.35$

Substituting the value of α to the above K_p expression $16.875 = \frac{0.35^2 P_T}{1-0.35^2}$

From which $P_T = 120.88\text{mmHg}$

Thus the total pressure would be 120.88mmHg.

On your own attempt to solve the question by using the given initial amount of 0.8moles

Example 23

The reactions between carbon monoxide and hydrogen proceed according to the following equation:
$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$

A dm^3 flask maintained at 700K, contain 0.1mole of carbon monoxide and suitable catalyst. When hydrogen is introduced into the flask until the equilibrium, the total pressure reaches 7atm and 0.06 moles of methanol is formed. Calculate the equilibrium constant, K_P.

Solution

	$CO\ (g)\ +$	$2H_2\ (g)$	$\rightleftharpoons$	$CH_3OH\ (g)$
Initially	0.1	a		0
At equilibrium	0.1 – x	a − 2x		x

$n_T = (0.1 - x) + (a - 2x) + x = 0.1 - 2x + a$

By Dalton's law of partial pressure; $P_T = P_{CO} + P_{H_2} + P_{CH_3OH}$

$$= \left(n_{CO} + n_{H_2} + n_{CH_3OH}\right)\frac{RT}{V}$$

Then $\frac{P_T V}{RT} = \left(n_{CO} + n_{H_2} + n_{CH_3OH}\right) = n_T$

So $\frac{7\times1}{0.082\times700} = 0.1 - 2x + a$

But $x = 0.06$

Then $0.122 = 0.1 - (2 \times 0.06) + a = n_T$ or $a = 0.142$

Thus the initial amount of H_2 was 0.142moles.

$$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} = \frac{X_{CH_3OH}P_T}{(X_{CO}P_T)(X_{H_2}P_T)^2} = \frac{\frac{n_{CH_3OH}}{n_T}P_T}{\left(\frac{n_{CO}}{n_T}P_T\right)\left(\frac{n_{H_2}}{n_T}P_T\right)^2} = \frac{n_{CH_3OH} \times {n_T}^2}{n_{CO} \times {n_{H_2}}^2 \times {P_T}^2}$$

But $n_{CH_3OH} = x = 0.06$ moles

$n_{CO} = 0.1 - x = 0.1 - 0.06 = 0.04$moles

$n_{H_2} = a - 2x = 0.142 - (2 \times 0.06) = 0.022$mole

$n_T = 0.122$moles

And $n_T = 7$atm

Substituting $K_p = \frac{0.06 \times 0.122^2}{0.04 \times 0.022^2 \times (7\text{atm})^2} = 0.94\text{atm}^{-2}$

Alternative solution:

	$CO\,(g) +$	$2H_2\,(g)$	$\rightleftharpoons$	$CH_3OH\,(g)$
Initially	0.1			0
At equilibrium	$0.1 - x$			x

But $x = 0.06\text{moles}$

Then:

$n_{CO} = 0.1 - x = (0.1 - 0.06)\text{moles} = 0.04\text{moles}$

$$P_{CO} = \frac{n_{CO}RT}{V} = \frac{0.04 \times 0.082 \times 700\text{atm}}{1} = 2.296\text{atm}$$

$$P_{CH_3OH} = \frac{n_{CH_3OH}RT}{V} = \frac{0.06 \times 0.082 \times 700}{1} = 3.444\text{atm}$$

At equilibrium: $P_T = P_{CO} + P_{H_2} + P_{CH_3OH}$ (From Dalton's law of partial pressure)

$7\text{atm} = 2.296\text{atm} + P_{H_2} + 3.444\text{atm}$

$P_{H_2} = 1.26\text{atm}$

$$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} = \frac{3.444\text{atm}}{(2.296\text{atm})(1.26\text{atm})^2} = 0.94\text{atm}^{-2}$$

Hence the equilibrium constant, K_p is 0.94atm^{-2}

Example 24

Ammonium hydrogen sulphide is allowed to dissociate into ammonia and hydrogen sulphide at 500K. At equilibrium the total pressure was measured to be 0.6atm. Calculate:

(i) The partial pressure of each.
(ii) The equilibrium constant, K_p.

Solution

	$NH_4HS\,(s)$	$\rightleftharpoons$	$NH_3(g)$ +	$H_2S\,(g)$
Initially	a		0	0
At equilibrium	$a - x$		x	x

That is at equilibrium $n_{NH_3} = n_{H_2S}$ and hence $P_{H_2S} = P_{NH_3} = P$

$$\left(\begin{array}{c}\text{As } P_{H_2S} = \dfrac{n_{H_2S}RT}{V} \text{ and } P_{NH_3} = \dfrac{n_{NH_3}RT}{V}; \\ \text{so if } n_{H_2S} = n_{NH_3} \text{then their respective partial pressures must be equal}\end{array}\right)$$

$$P_T = P_{NH_3} + P_{H_2S} = P + P = 2P; \text{thus } P = \frac{P_T}{2} = \frac{0.6\text{atm}}{2} = 0.3\text{atm}$$

(i) Hence the partial pressure of NH_3 is 0.3atm and the partial pressure of H_2S is 0.3atm.
(ii) $K_p = P_{NH_3} \times P_{H_2S} = 0.3\text{atm} \times 0.3\text{atm} = 0.09\text{atm}^2$

Hence the equilibrium constant, K_p is 0.09atm^2

Example 25

Given that $NH_4HS\,(s) \rightleftharpoons NH_3(g) + H_2S\,(g)$ and equilibrium constant is 0.108 atm^2. A sample of NH_4HS is introduced into evacuated flask where it dissociated and establishes the equilibrium. Calculate the total pressure exerted by the gases in the flask.

Solution

$K_p = P_{NH_3} \times P_{H_2S}$

But $P_{NH_3} = P_{H_2S} = P$

Then $K_p = P \times P = P^2$

$P = \sqrt{K_p} = \sqrt{0.108\text{atm}^{-2}} = 0.33\text{atm}$

By Dalton's law of partial pressure;

$P_T = P_{NH_3} + P_{H_2S} = 0.33\text{atm} + 0.33\text{atm} = 0.66\text{atm}$

Hence the total pressure exerted by gases in the flask is 0.66atm

Example 26

In the equilibrium: $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

3.2g of dinitrogen tetraoxide occupy a volume of 1dm^3 at 1×10^5Pa, and 25°C. Calculate:

(a) The degree of dissociation,
(b) The equilibrium constant, K_p.

Solution

Number of moles of $N_2O_4 = \frac{m}{M_r} = \frac{3.2}{92} = 0.035\text{moles}$

	$N_2O_4\ (g)$	$\rightleftharpoons$	$2NO_2\ (g)$
Initially	0.035		0
At equilibrium	0.035 – x		2x

$n_T = 0.035 - x + 2x = 0.035 + x$

By Dalton's law of partial pressure:

$$P_T = P_{N_2O_4} + P_{NO_2} = \frac{n_{N_2O_4}RT}{V} + \frac{n_{NO_2}RT}{V} = \left(n_{N_2O_4} + n_{NO_2}\right)\frac{RT}{V}$$

But $n_{N_2O_4} + n_{NO_2} = n_T$

Then $P_T = \frac{n_TRT}{V}$ or $n_T = \frac{P_TV}{RT} = \frac{10^5 \times 10^{-3}}{8.314 \times 298} = 0.04 = 0.035 + x$

From which; $x = (0.04 - 0.035)$ moles $= 0.005$moles

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}} = \frac{0.005}{0.035} = 0.14 \text{ or } 14\%$$

(a) Hence the degree of dissociation is 0.14 or 14%

	$N_2O_4\ (g)$	$\rightleftharpoons$	$2NO_2\ (g)$	
Initially	1		0	(Assuming initial amount of N_2O_4 is 1 mole)
At equilibrium	1 – α		2α	

$$n_T = 1 - \alpha + 2\alpha = 1 + \alpha;\ K_p = \frac{\left(P_{NO_2}\right)^2}{\left(P_{N_2O_4}\right)} = \frac{\left(X_{NO_2}P_T\right)^2}{\left(X_{N_2O_4}P_T\right)} = \frac{{X_{NO_2}}^2P_T}{X_{N_2O_4}}$$

Substituting values for mole fractions of NO_2 and N_2O_4 to above K_p expression gives:

$$K_p = \frac{4\alpha^2P_T}{1-\alpha^2} = \frac{4\times0.14^2\times10^5}{1-0.14^2}\text{Pa} = 7.9967 \times 10^3\text{Pa}$$

(b) Hence the equilibrium constant, K_p is $7.9967 \times 10^3 Pa$

Example 27

Consider the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g); K_p = 0.131atm$

A flask initially contains $N_2O_4(g)$ at 1.00atm pressure. Calculate the pressures of $NO_2(g)$ and $N_2O_4(g)$ at equilibrium.

Solution

Since partial pressures of gases, varies directly proportional to the number of moles,

$\text{mole ratio} = \text{pressure ratio}$

Thus pressures can be treated like moles as follows;

	$N_2O_4(g)$	$\rightleftharpoons 2NO_2(g)$
Pressure of each at $t = 0$	1	0
Pressure of each at equilibrium	$1 - x$	$2x$

Then $K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(2x)^2}{1-x} = \frac{4x^2}{1-x} = 0.131$

From which $4x^2 + 0.131x - 0.131 = 0$

Solving above equation gives practical value of x=0.165(x=-0.198 is ignored because pressure value cannot be negative)

Hence at equilibrium

Pressure of $N_2O_4 = 1 - x = 1 - 0.165 \text{ atm} = 0.835atm$

Pressure of $NO_2 = 2x = 2 \times 0.165 \text{ atm} = 0.33 \text{ atm}$

Example 28

A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.82L and heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 4×10^{-2}atm at this temperature.Calculate the mass of CaO present at equilibrium.

Solution

Given that; $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

From which;$K_P = P_{CO_2}$

Thus P_{CO_2} at 1000K was $4 \times 10^{-2}atm = K_p$

From ideal gas equilibrium; $n = \frac{PV}{RT}$

Thus number of moles of CO_2 at equilibrium will be given by;

$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{4\times10^{-2}\times0.82}{0.082\times1000}$ or 4×10^{-4}mol

Since initially there were no CO_2 in the container, number of moles of CO_2 produced in the reaction will be equal to the number of moles of the CO_2 at the equilibrium.

Thus n_{CO_2}produced in the reaction,$= 4 \times 10^{-4}$mol
From the stoichiometric of the reaction, mole ratio of CO_2 to CaO is 1:1

Thus n_{CO_2}produced=n_{CaO} produced= 4×10^{-4}mol
Using $m = nMr$; mass of CaO $= 4 \times 10^{-4} \times 56$ or0.0224g

Relationship between K_p and K_c

Consider the following system of homogeneous chemical equilibrium where by all regents are in gaseous phase.

$$aA\ (g)\ +\ bB\ (g)\ \rightleftharpoons\ cC\ (g)\ \ dD\ (g)$$

From which; $K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$

But from ideal gas equation: $PV = nRT$ or $P = \frac{nRT}{V}$; but $\frac{n}{V} = [\ \ ]$

So $P = [\ \ ]RT$

Substituting $P = [\ \ ]RT$ in above K_p expression:

$$K_p = \frac{([C]RT)^c([D]RT)^d}{([A]RT)^a([B]RT)^b} = \frac{[C]^c[D]^d(RT)^{c+d}}{[A]^a[B]^b(RT)^{a+b}}$$

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

c + d = Total number of molecules at products side for forward reaction

a + b = Total number of molecules at reactants side for forward reaction

Let $c + d = n$

$a + b = m$

Then $K_p = K_c\frac{(RT)^n}{(RT)^m}$

Hence $\mathbf{K_p = K_c(RT)^{n-m}}$ **or** $\mathbf{K_c = K_p(RT)^{m-n}}$

Example 29

0.04 moles of SO_3 was allowed to dissociate in 3 Litres vessel at 900K. At equilibrium the amount of SO_3 present is found to be 0.0284 moles

(i) Derive the relationship between K_c and K_p
(ii) Calculate K_c and K_p

Solution

Equation for the reaction is: $2SO_3\ (g)\ \rightleftharpoons\ 2SO_2\ (g)\ +\ O_2\ (g)$

$$K_p = \frac{\left(P_{SO_2}\right)^2\left(P_{O_2}\right)}{\left(P_{SO_3}\right)^2}$$

But from ideal gas equation: $PV = nRT$; $P = \left(\frac{n}{V}\right)RT$

But $\frac{n}{V} = [\ \ ]$; so $P = [\ \ ]RT$

Then $K_p = \frac{([SO_2]RT)^2([O_2]RT)}{([SO_3]RT)^2} = \frac{[SO_2]^2[O_2]RT}{[SO_3]^2}$

But $\frac{[SO_2]^2[O_2]}{[SO_3]^2} = K_c$

Hence $K_p = K_c\ RT$.

	$2SO_3\ (g)$	$\rightleftharpoons$	$2SO_2\ (g)$	$+\ O_2\ (g)$
Initially	0.04		0	0

At equilibrium $\quad 0.04 - 2x \qquad\qquad 2x \qquad\qquad x$

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{\left(\frac{2x}{V}\right)^2\left(\frac{x}{V}\right)}{\frac{(0.04-2x)^2}{V}}$$

But $\;0.04 - 2x = 0.0284$ (Amount of SO_3 remained at equilibrium) $= 0.0058$

$$\text{Thus } K_c = \frac{4 \times 0.0058^3}{(0.04 - (2 \times 0.0058))^2 \times 3} = 3.225 \times 10^{-4}\text{moldm}^{-3}$$

But from (i); $K_p = \; K_c\,RT$

Where $R = 0.082$ and $900K$.

Then $K_p = 3.225 \times 10 - 4 \times 0.0082 \times 900\text{atm} = 0.0238\text{atm}$

Hence $K_p = 0.0238\text{atm}$

Example 30

0.196g of nitrogen gas was reacted with 0.14g of hydrogen in 1 litre flask at 500K. At equilibrium the total pressure was found to be 10% less than the original pressure. Calculate:

(i) K_p for the reaction.
(ii) Percentage volume of each gas.

Solution

Using $n = \frac{m}{M_r}$

Number of moles of nitrogen gas $= \frac{0.196}{28}\text{moles} = 0.007\text{moles}$

Number of moles hydrogen gas $= \frac{0.14\text{moles}}{2} = 0.07\text{moles}$

	$N_2\,(g)$	$+\;3H_2\,(g)$	$\rightleftharpoons$	$2NH_3\,(g)$
Initially	0.007	0.07		0
At equilibrium	$0.007 - x$	$0.07 - 3x$		$2x$

$n_T = (0.007 - x) + (0.07 - 3x) + 2x = 0.077 - 2x$ (At equilibrium)

n_T before the reaction $= (0.007 + 0.07) = 0.077\text{moles}$

From ideals gas equation $P = \frac{nRT}{V}$

So before the reaction: $P_o = \frac{0.077RT}{V}$

At equilibrium $\qquad P_{eq} = \frac{(0.077-2x)RT}{V}$

But $P_{eq} = \frac{90}{100}P_o = 0.9P_o$

Then $\frac{0.9P_o}{P_o} = \frac{(0.077-2x)RT}{V} \div \frac{0.077RT}{V} = \frac{0.077-2x}{0.077} = 0.9$

$0.077 - 2x = 0.077 \times 0.9$

$2x = 0.0077; \quad x = 0.00385.$

From the equation for the reaction:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{0.007-x}{V}\right)\left(\frac{0.07-3x}{V}\right)^3} = \frac{V^2 \times 4x^2}{(0.007-x)(0.07-3x)^3}$$

$$= \frac{1 \times 4 \times 0.00385^2}{(0.007 - 0.00385)\big(0.07 - (3 \times 0.00385)\big)^3} = 94.26\text{dm}^6\text{mol}^{-2}$$

Using $K_p = K_c\,(RT)^{\,n-m}$

Where: n is the number of molecules in the products side = 2

m is the number of molecules in the reactants side = 4

$K_p = K_c\,(RT)^{\,2-4} = K_c\,(RT)^{\,-2}$

But $K_c = 94.26\ \text{dm}^6\ \text{mol}^{-2}$, $R = 0.082$, $T = 500K$

Thus $K_p = 94.26 \times (0.082 \times 500)^{-2}\ \text{atm}^{-2} = 0.056\text{atm}^{-2}$

Hence the Kp for the reaction is 0.056atm^{-2}

At equilibrium: $n_T = 0.077 - 2x = 0.077 - (2 \times 0.00385) = 0.0693\text{moles}$

Since volume ratio = mole ratio (The relationship is true only for gases according to Avogadro's law)

Then: $\%NH_3 = \frac{n_{NH_3}}{n_T} \times 100\% = \frac{2\times0.00385}{0.0693} \times 100\% = 11.11\%$

Thus the percentage of ammonia by volume is 11.11%

$$\%N_2 = \frac{n_{N_2}}{n_T} \times 100\% = \frac{(0.007 - x)}{n_T} \times 100\% = \frac{(0.007 - 0.00385)}{0.0693} \times 100\% = 4.5\%$$

Hence the percentage by volume of N_2 is 4.5%

$$\%H_2 = \frac{n_{H_2}}{n_T} \times 100\% = \frac{(0.07 - 3x)}{n_T} \times 100\% = \frac{\big(0.07 - (3 \times 0.00385)\big)}{0.0693} \times 100 = 84.34\%$$

Hence the percentage by volume of H_2 is 84.34%

Example 31

At 400°C the value of K_c for the reaction: $N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g)$ is $0.509\text{dm}^6\text{mol}^{-2}$.

If 2.5 moles of N_2, 7.5moles of H_2 were introduced into 2.5 Litres flask and in the pressure of catalyst allowed coming to equilibrium at 400°C. What would be the equilibrium concentration of each gas? What is the value of K_P for the reaction?

Solution

	$N_2\,(g)$	$+\ 3H_2(g)$	$\rightleftharpoons\ 2NH_3\,(g)$
Initially	2.5	7.5	0
At equilibrium	2.5 – x	7.5 – 3x	2x

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{2.5 - x}{V}\right)\left(\frac{7.5 - 3x}{V}\right)^3} = \frac{V^2 \times 4x^2}{(2.5 - x)\big(3(2.5 - x)\big)^3}$$

Thus $K_c = \frac{V^2\times4x^2}{27(2.5-x)^4} = 0.509$

Then $\sqrt{\frac{V^2\times4x^2}{27(2.5-x)^4}} = \sqrt{0.509}$; $\frac{V\times2x}{5.196(2.5-x)^2} = 0.713$

Substituting V = 2.5L and simplifying above equation gives;

$3.7x^2 - 23.52x + 23.155 = 0$; $x = 1.22$

Using $[\quad] = \frac{n}{V}$

Thus at equilibrium:

$[N_2] = \frac{2.5 - x}{V} = \frac{2.5 - 1.22}{2.5} = 0.512M$

$[H_2] = \frac{7.5 - 3x}{V} = \frac{7.5 - (3 \times 1.22)}{2.5} = 1.536M$

$[NH_3] = \frac{2x}{V} = \frac{2 \times 1.22}{2.5} = 0.976M$

$K_p = K_c(RT)^{n-m}$ where $n = 2$ and $m = 4$

Then $K_p = 0.509 \times (0.082 \times 673)^{-2}atm^{-2} = 1.67 \times 10^{-4}atm^{-2}$

The K_p for the reaction is $1.67 \times 10^{-4}atm^{-2}$

Example 32

A1200°C, the following equilibrium is established between chlorine atoms and molecules;

$$Cl_2(g) \rightleftharpoons 2Cl(g)$$

The composition of the equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pin hole. It is found that at 1200°C and 1atm pressure; the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant, K_c

Solution

If M_m and M_{Kr} represents molar mass of the mixture and krypton respectively,

And R_m and R_{Kr} represents rate of diffusion of the mixture and krypton respectively

Then $\frac{R_{Kr}}{R_m} = \sqrt{\frac{M_m}{M_{Kr}}}$

Or $M_m = M_{Kr}\left(\frac{Rkr}{Rm}\right)^2$

But $\frac{Rm}{Rkr} = 1.16$ or $\frac{R_{Kr}}{R_m} = \frac{1}{1.16}$

Then $M_m = 84 \times \left(\frac{1}{1.16}\right)^2 = 62.4257g/mol$

Considering the dissociation of Cl_2;

Van't Hoff's factor, $i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{71}{62.4257} = 1.1374$

And degree of dissociation, $\alpha = \frac{i-1}{N-1} = \frac{1.1374-1}{2-1} = 0.1374$

It follows that: $Cl_2(g) \rightleftharpoons 2Cl(g)$

At equilibrium; $1 - \alpha \qquad 2\alpha$

$K_p = \frac{(P_{Cl})^2}{P_{Cl_2}} = \frac{(X_{Cl}P_T)^2}{X_{Cl_2}P_T} = \frac{(X_{Cl})^2\,P_T}{X_{Cl_2}}$

But $X_{Cl} = \frac{n_{Cl}}{n_T} = \frac{2\alpha}{1+\alpha} = \frac{2\times0.1374}{1+0.1374} = 0.2416$

And $X_{Cl_2} = \frac{n_{Cl_2}}{n_T} = \frac{1-\alpha}{1+\alpha} = \frac{1-0.1374}{1+0.1374} = 0.7584$

Substituting $K_p = \frac{(0.2416)^2\times1atm}{0.7584} = 0.077atm$

Using $K_c = K_p(RT)^{m-n} = 0.077 \times (0.82 \times 1473)^{-1}moldm^{-3} = 6.37 \times 10^{-4}moldm^{-3}$

Hence the equilibrium constant,$K_c = 6.37 \times 10^{-4}moldm^{-3}$

Reaction quotient (Q)

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient**. The reaction quotient, *is the ratio of product of concentration of products to that of reactants raised to power equal to their stoichiometric coefficients obtained in the course of the chemical reaction*.

The quotient is useful in determination of the **position of the chemical equilibrium** (*the direction to which the reaction proceeds more so as to establish the equilibrium*) by comparing its value with that of the equilibrium constant at given temperature. Like equilibrium constant, the reaction quotient is derived directly from the stoichiometry of the balanced equation and for gases, it can be written in terms of partial pressures as well.

If: $\mathrm{aA + bB \quad \rightleftharpoons \quad cC + dD}$

Then, $\mathrm{Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}}\left(\text{or } \mathrm{Q_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}}\right)$

- When $\mathrm{Q_c < K_c}$, the position of the chemical equilibrium shifts to the right (product side), that is; more product will be formed to establish equilibrium.
- When $\mathrm{Q_c > K_c}$, the position of the chemical equilibrium shifts to the left (reactant side), that is; more reactant will be formed to establish equilibrium.
- When $\mathrm{Q_c = K_c}$, the reaction is at equilibrium.

The reader should recognise the difference in the meaning of '[ ]' as used in equilibrium constant expression and in reaction quotient expression:

- In equilibrium constant, $\mathrm{K_c}$ expression, '[ ]' stands for molar equilibrium concentration i.e. the concentration of reagent (s) when the system is at equilibrium.
- In reaction quotient, $\mathrm{Q_c}$ expression '[ ]' stands for molar concentration at any time in the course of the chemical reaction, i.e. the system not necessary to be at equilibrium.

Example 33

At 450°C, $\mathrm{Q_c}$ for hydrogen iodide synthesis is 50.5.You place 1×10^{-2} moles of hydrogen, 3×10^{-2} moles of iodine and 2×10^{-2}moles of hydrogen iodide in a 2 litres container at 450°C. In which direction the reaction.

$\mathrm{H_2\,(g) + I_2\,(g) \quad \rightleftharpoons \quad 2HI\,(g)}$ proceed in order to reach the equilibrium

Solution

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2\times10^{-2}}{V}\right)^2}{\left(\frac{1\times10^{-2}}{V}\right)\left(\frac{3\times10^{-2}}{V}\right)} = 1.33$$

But $K_c = 50.5$; thus $Q_c < K_c$

Hence the reaction will proceed to the right hand side to reach the equilibrium.

Example 34

The solution containing $0.2M$ of Fe^{2+}, $0.1M$ of Ag^{+} and $0.5M$ of Fe^{3+} were mixed together with silver and the reaction was left to establish the equilibrium. Calculate the percentage of each reagent in the solution at equilibrium if the equilibrium reaction is formed as follows:

$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$; Given that $K_c = 4$

Solution

Calculating Q_c so as to determine the position of chemical equilibrium,

$$Q_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]} = \frac{0.5}{0.2\times0.1} = 25$$

But $K_c = 4$

Thus $Q_c > K_c$ and hence the position of the chemical equilibrium shift to the left so as to establish the equilibrium (backward reaction is more favoured)

	$Fe^{2+}(aq)$	$+ Ag^{+}(aq)$	$\rightleftharpoons$	$Fe^{3+}(aq)$	$+ Ag(s)$
Initially	0.2	0.1		0.5	
At equilibrium	$0.2 + x$	$0.1 + x$		$0.5 - x$	

$$K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]} = \frac{0.5 - x}{(0.2 + x)(0.1 + x)} = \frac{0.5 - x}{x^2 + 0.3x + 0.02} = 4$$

(Here there is no need of dividing by the volume because we have already given with number of moles in one litre of the solution for each reagent i.e. molarity of each reagent)

$4x^2 + 1.2x + 0.08 = 0.5 - x$ or $4x^2 + 2.2x - 0.42 = 0$; $x = 0.15$

$n_{Fe^{2+}} = 0.2 + x = (0.2 + 0.15)$ moles $= 0.35$moles

$n_{Ag^{+}} = 0.1 + x = (0.1 + 0.15)$ moles $= 0.25$moles

$n_{Fe^{3+}} = 0.5 - x = (0.5 - 0.15)$ moles $= 0.35$moles

$n_T = (0.35 + 0.25 + 0.35)$ moles $= 0.95$moles

$$\%Fe^{2+} = \frac{n_{Fe^{2+}}}{n_T}\times100\% = \frac{0.35}{0.95}\times100\% = 36.842\%$$

$$\%Ag^{+} = \frac{n_{Ag^{+}}}{n_T}\times100\% = \frac{0.25}{0.95}\times100\% = 26.316\%$$

$$\%Fe^{3+} = \frac{n_{Fe^{3+}}}{n_T}\times100\% = \frac{0.35}{0.95}\times100\% = 36.842\%$$

Hence: Percentage of Fe^{2+} is 36.842%

Percentage of Ag^{+} is 26.316%

Percentage of Fe^{3+} is 36.842%

DIGGING DEEPER EXERCISE 13

EXERCISE 13A: BINDER QUESTIONS

Question 1

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

Sketch the graph of concentration of reactants and products against time for the above hypothetical reversible reaction which attain chemical equilibrium with:

(a) $K_c > 1$
(b) $K_c < 1$
(c) $K_c = 1$

Question 2

When added to $Fe_3O_4(s)$ in a closed container, which one of the following substances; $H_2(g), H_2O(g)$ or $O_2(g)$ will allow equilibrium to be established in the following reaction:

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_3(s) + 4H_2(g)$

Question 3

For the reaction $A_2 + 2B \rightleftharpoons 2AB$, the rate of the forward reaction is 18M/s and the rate of the reverse reaction is 12M/s. The reaction is not at equilibrium. Will the reaction proceed in the forward or reverse direction to attain equilibrium?

Question 4

The following reaction occurs when a burner on a gas stove is lit:

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

Question 5

List down at least five defining traits of chemical equilibrium.

Question 6

The equilibrium constant for synthesis of hydrogen chloride, hydrogen bromide and hydrogen iodide are given below:

$H_2 + Cl_2 \rightleftharpoons HCl, \quad K_c = 10^{17}$

$H_2 + Br_2 \rightleftharpoons HBr, \quad K_c = 10^{9}$

$H_2 + I_2 \rightleftharpoons HI, \quad K_c = 10$

(i) What do the values of K_c tell you about the extent of each reaction?
(ii) Which of these reactions you would regard as complete conversion?

Question 7

Giving reasons argue for or against the statement that, "reactions with large equilibrium constants are very fast."

Question 8

Why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

Question 9

Write the equilibrium constant expression for K_c for each of the following reactions;

(a) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$
(b) $SnO_2(s) + 2CO(g) \rightleftharpoons Sn(s) + 2CO_2(g)$
(c) $Cr(s) + 3Ag^+(aq) \rightleftharpoons Cr^{3+}(aq) + 3Ag(s)$
(d) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4 + 4H_2(g)$

Question 10

Write the equilibrium constant expression for the following reactions:

(i) $N_2H_4\,(g) + O_2(g) \rightleftharpoons N_2\,(g) + 2H_2O(g)$
(ii) $3Fe\,(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
(iii) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$
(iv) $Cr(s) + 3Ag^+(aq) \rightleftharpoons Cr^{3+}(aq) + 3Ag(s)$

Question 11

Most metal ions combine with other ions in solution for example in aqueous ammonia; silver (I) ions are in equilibrium with different complex ions.

$$[Ag(H_2O)_2]^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + 2H_2O(l)$$

A room temperature, K_c for this reaction is 1×10^7. Which of the two silver complex ions is the more stable? Give a reason for your choice.

Question 12

Each of the following mixture was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium? $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.

In each case, provide an explanation for your answer.

(i) Pure $CaCO_3$
(ii) CaO and a CO_2 pressure greater than the value of K_p
(iii) Some $CaCO_3$ and a CO_2 pressure greater than the value of K_p
(iv) $CaCO_3$ and CaO

Question 13

For the formation of NH_3 from N_2 and H_2:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); K_p = 4.34 \times 10^{-3}\,atm^{-2} \text{ at } 300°C$$

What is the value of K_p for the reverse reaction?

Question 14

The equilibrium constant for the reaction of N_2 with O_2 to form NO equals $K_c = 1 \times 10^{-30}$ at 25°C. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g); K_c = 1 \times 10^{-30}$

Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction: $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

Question 15

Identify each reaction as essentially going to completion or not taking place

(a) $N_2(g) + 3Cl_2(g) \rightleftharpoons 2NCl_3(g)$ $K_c = 3.0 \times 10^{11}$
(b) $2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g)$ $K_c = 9.5 \times 10^{-13}$
(c) $2NO(g) + 2CO(g) \rightleftharpoons N_2(g) + 2CO_2(g)$ $K_c = 2.2 \times 10^{59}$

Question 16

Consider the following reaction equation:

$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g);\ K_p = 28.4\,atm^{-1}$ at 298K.

In the reaction mixture at equilibrium, the partial pressure of NO is 108 torr and that of Br_2 is 126 torr. What is the partial pressure of NOBr in this mixture?

Question 17

The equilibrium constant (K_c) for the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 4.63×10^{-3} at 25°C.

What is the value of K_p for this reaction at this temperature?

Question 18

For the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); K_P = 4.3 \times 10^{-4}(-375°C)$. Calculate K_c for this reaction.

Question 19

Anhydrous calcium chloride often used as a desiccant. In the presence of excess of $CaCl_2$, the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85} atm^{-6}$ for the following reaction at room temperature:

$$CaCl_2(s) + 6H_2O(g) \rightleftharpoons CaCl_2.6H_2O(s)$$

What is the equilibrium vapour pressure of water in a vessel that contains $CaCl_2(s)$?

Question 20

The vapour pressure of water at 25°C is 0.0313atm. Calculate the value of K_p and K_c at 25°C for the following equilibrium:

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

EXERCISE 13B: REAL QUESTIONS

Question 21

With a help of an equation in each case, give two examples of chemical equilibrium in the real daily life.

Question 22

Inside the sealed Pepsi soda, not all carbon dioxide molecules are dissolved in the water; some molecules escape from the solution in the gaseous form. So there is carbon dioxide gas residing between the liquid solution and the cap. However, if we look at the bottle, these undissolved gas molecules are not observed; explain why?

Question 23

The concept of equilibrium is not only applicable for chemical changes, physical changes, such as phase transitions, are also reversible and may establish equilibria too. Evaporation of water of in a closed container is a good example of this we are witnessing in a daily life.

(i) Explain clearly how the physical equilibrium is achieved during the evaporation of water.
(ii) Which is the physical quantity that is resulted from the evaporation is equivalent to equilibrium constant? Give reason(s) to justify your answer.
(iii) Compare and contrast the physical equilibrium and chemical equilibrium.

Question 24

Haemoglobin (Hb) carries oxygen inside the human body according to the following equation:

$$Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq) \text{............(i)}$$

The haemoglobin may also carry carbon monoxide inside the human body according to the following equation:

$$Hb(aq) + 4CO(g) \rightleftharpoons Hb(CO)_4(aq) \text{............(ii)}$$

It is known that equilibrium constant for the second reaction is much higher than that of the first reaction.

(i) Between haemoglobin-oxygen bond and haemoglobin-carbon monoxide bond, which one is stronger? Give reason.
(ii) If one is subjected to equal concentration of both oxygen gas and carbon monoxide gas, which gas will be consumed more?

Question 25

Your friend **Kipute**, was asked to solve the following problem:

Consider the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g): K_p = 1.45 \times 10^{-5}\ at\ 500°C$$

In equilibrium mixture of the three gases at 500°C, *the partial pressure of* H_2 *is 0.928atm and that of* N_2 *is 0.432atm. What is the partial pressure of* NH_3 *in the equilibrium mixture.*

After solving, she found $P_{NH_3} = 2.24 \times 10^{-2}$atm. How could you help your friend to recognise that the answer is wrong without re-working the problem?

Question 26

Kipute was asked to calculate the least amount of acetic acid and she found the mass of 1.8g. Without re-working the problem, how could you show that the answer she got was correct? The problem was:

12g of acetic acid is heated with 18.6g of ethanol in $1dm^3$ *flask at 298K. Calculate the least amount of acetic acid which may be present in the flask under these conditions if the equilibrium constant is 4.2.*

Question 27

Mr. Akilikubwa aimed to design a chemical reaction that he would use to prepare at least 5g of lime from limestone. He wanted to achieve this by heating 20g of limestone in a sealed container of volume 5L to 800℃. The equilibrium constant for the thermal decomposition of limestone at this temperature is 1.16atm.

(i) Was **Mr. Akilikubwa** successful in his design?
(ii) Would the amount of lime increase by adding more limestone? Give a reason based on your calculation.
(iii) Would the amount of lime increase or decrease or remain the same by using a sealed container of larger volume? Give a reason based on your calculation.

Question 28

Mr. Akilikubwa aimed to design a chemical reaction that he would use to prepare a sample of lime from limestone. He wanted to achieve this by heating a sample of limestone in a closed vessel of volume 10L to 800℃. However, he is bothered by the fact that the decomposition of limestone is reversible, so he would have extra work of separating lime from limestone after completing the preparation. The equilibrium constant for the thermal decomposition of limestone at this temperature is 1.16atm.

(i) What maximum amount of limestone would **Mr. Akilikubwa** put in the vessel without a worry of having the extra duty of separation?
(ii) What mass of lime will be obtained as the only solid substance in the vessel?

EXERCISE 13C: HOT QUESTIONS

Question 29

Consider the following reaction: $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

At certain temperature, $K_c = 8.5 \times 10^{-3}$. A reaction mixture at this temperature containing solid NH_4HS has $[NH_3] = 0.166M$ and $[H_2S] = 0.166M$. Will more of the solid form or will some of the existing solid decompose as equilibrium is reached?

Question 30

Nitrogen dioxide dimerises according to the following equation;

$$2NO_2(g) \rightleftharpoons N_2O_4(g); K_P = 6.7atm^{-1} \text{ at } 298K$$

A 2.25L container contains 0.55mol of NO_2 and 0.082mol of N_2O_4 at 298K. Is the reaction at equilibrium? If not, in what direction will the reaction proceed?

Question 31

A 700k, carbon monoxide reacts with water to form carbon dioxide and hydrogen:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

The equilibrium constant for this reaction at 700K is 5.1 considers an experiment in which 1.00mol of $CO(g)$ and 1.00mol of $H_2O(g)$ are mixed together in a 1.00L flask at 700K.Calcualte the concentrations of all species at equilibrium.

Question 32

Sulphur trioxide decomposes at high temperature in a sealed container;

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

Initially, the vessel is charged at 1000K with $SO_3(g)$ at a partial pressure of 0.500atm. At equilibrium, the SO_3 partial pressure is 0.200atm.Calculate the value of K_p at 1000K.

Question 33

At temperature near 800℃, steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

The mixture of gases that results is an important industrial fuel called **water gas**

(a) At 880°C, the equilibrium constant for this reaction is $K_p = 14.1$.What are the equilibrium partial pressures of H_2O,CO and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100mol of H_2O in a 1L vessel?
(b) What is the minimum amount of carbon required to achieve equilibrium under these conditions?
(c) What is the total pressure in the vessel at equilibrium?

Question 34

20g Of $CaCO_3(s)$ were placed in a closed vessel, heated and maintained at 727°C under equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g);$$

And it is found that 75% of $CaCO_3$ was decomposed if the volume of the container was 15L, calculate the value of K_p.

Question 35

The equilibrium constant for the reaction is 9.40 at 900°C

$$S_2(g) + C(s) \rightleftharpoons CS_2(g)$$

When 1.42atm of S_2 and excess of $C(s)$ come to equilibrium; partial pressure of which component changes to the maximum and of which one changes to the minimum and hence calculate their values.

Question 36

An analysis of the gaseous phase ($S_2(g)$ and $CS_2(g)$) present at equilibrium at 1000°C in the reaction;

$C(s) + S_2(g) \rightleftharpoons CS_2(g)$; shows it to be 13.71% C and 86.29% S, by mass. What is K_c for this reaction?

Question 37

The reaction: $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$, is at equilibrium at temperature in which the equilibrium constant, K_c, is $375\ mol^{-1}dm^3$ The equilibrium amount of oxygen found in a 0.755litre containing this equilibrium mixture is 0.148 mol .What is the ratio of [NO] to$[NO_2]$ in this equilibrium mixture.

Question 38

At temperature close to 400°C, hydrogen iodide has a degree of dissociation of 20%. Calculate the composition of the equilibrium mixture produced if 1mole of hydrogen and 2.1mole of iodine react to equilibrium at this temperature.

Question 39

At a certain temperature, the equilibrium pressures of steam and hydrogen in contact with iron and its black oxide Fe_3O_4 were found to be $1533Nm^{-2}$ (11.5mmHg) and $32190Nm^{-2}$(241.5 mmHg) respectively. Calculate:

(a) The pressure of hydrogen in equilibrium with 1066 Nm^{-2} (8 mmHg) of steam pressure.
(b) The pressure of hydrogen and steam at a total pressure of 101300 Nm^{-2}(760mmHg) at this temperature. Equation for the reaction is $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(S)} + 4H_{2(g)}$

Question 40

The equilibrium constant of the reaction: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ at 1000°C is 1.6. What is the percentage by volume of each gas in the equilibrium mixture at 1000°C produced from:
(a) A mixture of $50cm^3$ hydrogen and $50cm^3$ carbon dioxide.
(b) $25cm^3$ each of carbon dioxide and monoxide and $50cm^3$ of hydrogen.

Question 41

0. 5 moles of hydrogen gas and 0.5 moles of iodine gas react in a 10L evacuated vessel at 440°C, hydrogen iodide is formed. The equilibrium constant, K_C for the reaction at 440°C is 50.

(i) Calculate the value of K_p
(ii) Calculate number of moles of I_2 remain unreacted at equilibrium

Question 42

1 mole of H_2, 2moles of I_2 and 3moles of HI are injected in 1L vessel. What will be the concentration of H_2, I_2 and HI at equilibrium at 490 °C? (The equilibrium constant for the reaction at 490°C is 45.9).

Question 43

5g of PCl_5 were completely vapourised at 250°C in a vessel of 1.9L capacity. The equilibrium mixture exerted a pressure of 1atm. Calculate:

(i) The degree of dissociation.
(ii) K_c and K_p for the reaction.

Question 44

What will be percentage of dissociation when 1 mole of H_2S gas is introduced in a vessel of 1.1L at 1000K? The value of K_c for the reaction is 10^{-6}.

Question 45

Calculate the value of K_P at 700K for each of the reaction represented below;

(i) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$
(ii) $2H_2S(g) + N_2(g) + 3H_2(g) \rightleftharpoons 2NH_4HS(g)$

Given that:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3; \quad K_P = 3.1 \times 10^{-4} \text{ at } 700K$$

$$NH_3(g) + H_2s(g) \rightleftharpoons NH_4HS(g); \quad K_P = 8.3 \times 10^{-3} \text{ at } 700K$$

Chapter 14

FACTORS AFFECTING POSITION OF CHEMICAL EQUILIBRIUM

LE CHATELIER'S PRINCIPLE

Equilibrium plays a very important role in the study of chemical reactions as it tells us about the direction of chemical reactions. The equilibrium helps us to control the reaction conditions to favour formation of desired products. In order to have that control, it is important to understand factors which affect equilibrium position.

There are three common factors which affect position of chemical equilibrium, namely;

- Concentration
- Pressure
- Temperature

The effect of mentioned factors on position of chemical equilibrium is generally explained by **Le Chatelier's principle** which states that, *"If a chemical system is in equilibrium and one of the factors involved in the equilibrium is altered, the equilibrium will shift so as to tend to annul the effect of the change"*

CONCENTRATION AND POSITION OF CHEMICAL EQUILIBRIUM

General rule derived from Le Chatelier's principle:

Change in concentration of reagent(s) involved in system of chemical equilibrium, shifts the position of chemical equilibrium to the side of lower concentration.

The effect of change in concentration on position of chemical equilibrium can also well explained by the concept of **reaction quotient, $\mathbf{Q_c}$** as done below:

Consider the following chemical system of reversible reaction: $aA + bB \rightleftharpoons cC + dD$

If the chemical system is at equilibrium; $\mathbf{Q_c = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}}$

If concentration of A or B is lowered, denominator in the above expression is decreased thus making, $Q_c > K_c$ and hence the position of chemical equilibrium shifts to the left i.e. reverse reaction become more favoured.

If concentration of C or D is increased, numerator in the above expression is increased thus making, $Q_c > K_c$ and hence the position of chemical equilibrium shifts to the left i.e. reverse reaction become more favoured.

If concentration of C or D is lowered, numerator in the above expression is decreased thus making $Q_c < K_c$ and hence position of chemical equilibrium shifts to the right.

If concentration of A or B increased, denominator in the above expression is increased thus making $Q_c < K_c$ and hence position of chemical equilibrium shifts to the right.

The reader should remember that: change in concentration has no effect on the value of equilibrium constant (K_c), it is only alters the reaction quotient (Q_c).

PRESSURE AND POSITION OF CHEMICAL EQUILIBRIUM

When chemical system is at equilibrium and the pressure of the system is increased or decreased, Le Chatelier's principle requires the position of chemical equilibrium to shift so as to decrease the added pressure or to increase the pressure respectively in order to re-store the equilibrium.

General rule

If the chemical system is in equilibrium and the pressure of the system is increased the position of chemical equilibrium shifts to the side of lower volume i.e. to the side with fewer gaseous molecules while decreasing pressure of the system shifts position of chemical equilibrium to the side of greater volume i.e. to the side with greater number of gaseous molecules.

To understand the concept, consider the following case of formation of ammonia from its constituent gaseous elements according to the following equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

From the above equation:

- **Four** gaseous molecules (**one** molecule of nitrogen molecule and **three** hydrogen molecules) react to give **two** gaseous molecules of ammonia.
- Thus the forward reaction is accompanied by decrease in number of gaseous molecules from **four** to **two.** *In other words, we can say that the forward reaction is accompanied by decrease in volume because according to Avogadro's law, volume of gases varies directly proportional to their number of molecules.*
- Since pressure exerted by the gas at given temperature increase with an increase of number of gas molecules; from the above fact we can conclude that the *forward reaction is accompanied by decrease in pressure and the reverse reaction is accompanied with increase in pressure.*
- Thus if the chemical system is at equilibrium and the pressure of the system is increased, to lower the added pressure the reaction must proceed in forward direction i.e. equilibrium shifts to the side of lower volume while if the pressure is decreased, to increase the pressure the reaction must proceed in backward direction i.e. equilibrium shifts to the side of greater volume.

For better understanding on the concept of effect of pressure on position of chemical equilibrium, you should understand the following facts in addition to the above explained facts:

- The greater the volume difference (difference in number of gaseous molecules between products side and reactants side), the greater effect the pressure has on position of chemical equilibrium.
- Pressure has no effect on position of chemical equilibrium in systems which do not involve gaseous reagents because liquid state is less compressible while solids are uncompressible.
- Changing pressure has no effect on position of chemical equilibrium of reaction with gaseous reagents without involving the change in volume i.e. reactions which do not involve the change in number of gaseous molecules from reactants side to products side.
- Pressure has effect on position of chemical equilibrium which involves gaseous reagent(s) accompanied with change in volume from the reactants to products side.
- Effect of pressure is the special case of effect of concentration in chemical system which involves gaseous reagents as for gases; the pressures varies directly proportional to their concentration. So like concentration, effect of pressure can be explained by using reaction quotient, R_Q and then comparing the quotient with K_p
- Like concentration, changing in the pressure has no effect on the value of equilibrium constant, K_p

TEMPERATURE AND POSITION OF CHEMICAL EQUILIBRIUM

The effect of temperature is well explained by **Vant Hoff's law of mobile** which states that, *"Increase in temperature and decrease in temperature favours forward reaction for endothermic reaction and exothermic reaction respectively and vice versa"*

The simpler way to understand this!

- For endothermic reaction, heat must be supplied to the system for the reaction to occur. Thus the heat may be regarded as the reactant for the reaction.

  That is: $\text{reactants} + \text{heat} \rightleftharpoons \text{products}$
- So if heat is added by raising temperature, the equilibrium will shift to the right to eliminate the added heat and if it is decreased, the equilibrium will shift to the left to compensate the reduced heat.

- For exothermic reaction, heat is evolved after the reaction. Thus the heat may be regarded as the product for the reaction.

  That is: $\text{reactants} \rightleftharpoons \text{products} + \text{heat}$

- So if the heat is added by raising temperature, the equilibrium will shift to the left to eliminate the added heat and if it is decreased the equilibrium will shift to the right to compensate the reduced heat.

So the most useful ability in understanding the effect of temperature on position of chemical equilibrium is the ability to identify **endothermic** and **exothermic reaction.**

Identification of endothermic and exothermic chemical reactions

This can be done by studying:

- Thermo-chemical equation
- Energy profile diagram

By studying thermo-chemical equation

This can simply be done by considering the sign of heat of reaction:

- If the heat of reaction is **positive,** then the reaction is **endothermic**.
- If the heat of reaction is **negative,** then the reaction is **exothermic**.

By studying energy profile diagram

There is a limit of potential energy below which no reaction will take place and the energy barrier is known as **activation energy**. So at initial stages of reaction the potential energy must increase until the activation energy is attained.

Once the activation energy has been attained, there is a formation of an intermediate product which is known as **activated complex**, e.g. for the reaction; $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$, the activated complex is H_2Cl_2.

So if the energy is sufficient the new product (HCl in the above example) is formed but if it is insufficient the activated complex disintegrates to the original reactants (H_2 and Cl_2) and no reaction will occur.

If the energy is sufficient, the final product is formed by the activated complex starting to releasing energy to the surroundings so as to get new stability of new compound. The final potential energy of final product is what determines whether the reaction is endothermic or exothermic. **If the potential energy of the product is greater than that of reactants (which was assumed to be zero) then the reaction is endothermic and if it is less, the reaction become exothermic**.

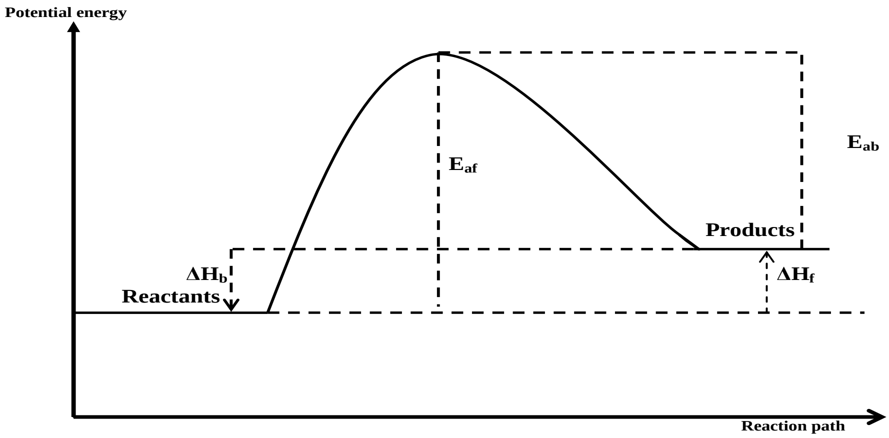


Figure 14.1 Energy profile diagram for endothermic chemical reaction

Where:

$\mathbf{E_{af}}$ and $\mathbf{E_{ab}}$ are activation energies for forward and backward reaction respectively (for endothermic reaction, $E_{af} > E_{ab}$)

$\mathbf{\Delta H_f}$ and $\mathbf{\Delta H_b}$ are heats of reactions for forward and backward reactions respectively

It should be noted that (as seen from the figure above), heat of reaction for forward and backward reaction are equal in magnitude but opposite in sign. If the forward reaction is endothermic then the backward reaction is exothermic and vice-versa.

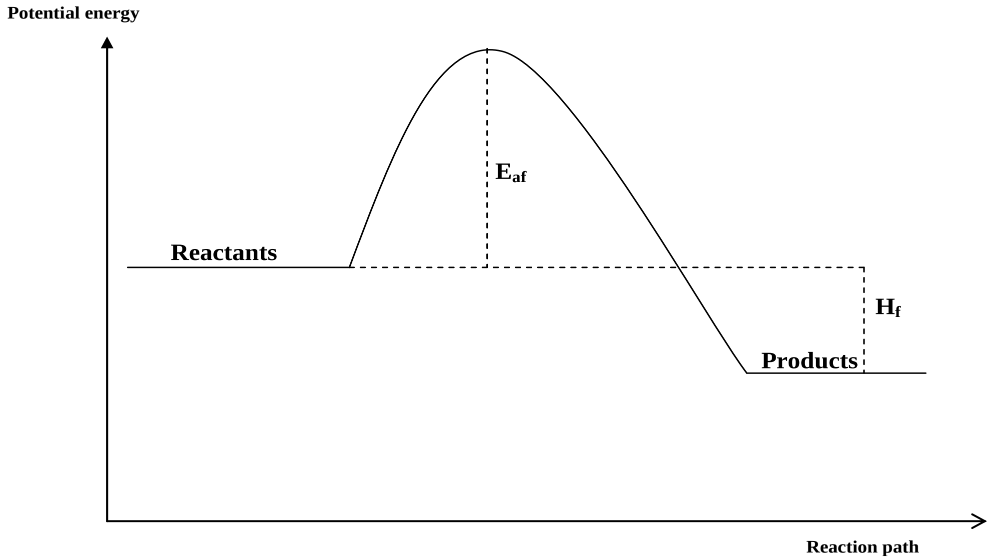


Figure 14.2 Energy profile diagram for exothermic chemical reaction

Note: in this case of exothermic reaction, $E_{af} < E_{ab}$ in contrast to endothermic reaction where $E_{af} > E_{ab}$

The reader should understand that:

Temperature is the only factor which can change the position of chemical equilibrium by changing the value of equilibrium constant.

Position of chemical equilibrium of reactions with greater magnitude of heat of reaction is more affected by change in temperature than those with smaller value of the magnitude.

Change in temperature has negligible effect on the position of the chemical equilibrium in reaction whose magnitude of heat of reaction is close to zero.

Kinetics of effect of temperature on the position of chemical equilibrium

Recall: $K_c = \frac{k_f}{k_b}$

If K_c' is the equilibrium constant at T_1 where corresponding rate constants are k_f' and k_b' for forward and backward reaction respectively;

And K_c'' is the equilibrium constant at T_2 where corresponding rate constants are k_f'' and k_b'' for forward and backward reaction respectively;

That is $K_c' = \frac{k_f'}{k_b'}$ and $K_c'' = \frac{k_f''}{k_b''}$

Then from the Arrhenius equation: $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

Or $\quad k_2 = k_l \ln^{-1}\left(\frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right)$

Therefore:

$$k_f'' = k_f' \ln^{-1}\left(\frac{E_{af}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right)$$

$$k_b'' = k_b' \ln^{-1}\left(\frac{E_{ab}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right)$$

Where E_{af} and E_{ab} are activate energies for forward and backward reaction respectively. Now to make things look simpler, let:

$$\ln^{-1}\left(\frac{E_{af}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right) = n_1$$

And $\quad \ln^{-1}\left(\frac{E_ab}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)\right) = n_2$

Then $K_c'' = \frac{k_f' \times n_1}{k_b' \times n_2}$; but $\frac{k_f'}{k_b'} = K_c'$

And therefore $\mathbf{K_c'' = \frac{n_1}{n_2} K_c'}$

Now consider the following two cases;

First case: The temperature is increased from T_1 to T_2

For endothermic reaction, $E_{af} > E_{ab}$

That means that $n_1 > n_2$ and $\frac{n_1}{n_2} > 1$

Hence $K_c'' > K_c'$ for endothermic reaction.

To conclude; increase in temperature increases K_c value for endothermic reaction and thus shifts the position of chemical equilibrium to the right. This result agrees with the result from Le-Chatelier's principle as explained earlier.

For exothermic reaction, $E_{af} < E_{ab}$

That means that $n_1 < n_2$ and therefore $\frac{n_1}{n_2} < 1$

Hence $K_c'' < K_c'$ for exothermic reaction.

To conclude; increase in temperature decreases K_c value of exothermic reaction and thus shifts the position of chemical equilibrium to the left. Again this result agrees with Le-Chatelier's principle.

Second case: The temperature is decreased from T_1 to T_2

For exothermic reaction, $E_{af} > E_{ab}$

Since now $T_1 - T_2$ is negative number, $n_1 < n_2$ and therefore $\frac{n_1}{n_2} < 1$

Hence $K_c'' < K_c'$ indicating that the new equilibrium has shifted to the left as result of decrease in temperature in the endothermic reaction.

For exothermic reaction, $E_{af} < E_{ab}$

Again as $T_2 - T_1$ is negative number, $n_1 > n_2$ and therefore $\frac{n_1}{n_2} > 1$

Hence $K_c'' > K_c'$ indicating that the new equilibrium has shifted to the right as result of decreasing temperature in the exothermic reaction.

CATALYST AND CHEMICAL EQUILIBRIUM

Catalyst affects how fast equilibrium is achieved (with catalyst, the equilibrium is achieved sooner) but does not affect equilibrium position, why? This is because the forward and backward (reverse) reactions pass through the same transition state, the catalyst lowers the activation energy barrier for the forward and backward reaction by the same amount. The catalyst therefore increases the rate of forward and backward reaction by the same factor, and the composition of the equilibrium mixture is unchanged.

- Because a catalyst has no effect on the equilibrium concentration, it does not appear in the balanced equation or in the equilibrium constant expression.

Catalysts decrease the activation energy of both forward and backward reaction by equal amount as illustrated in the figure below.

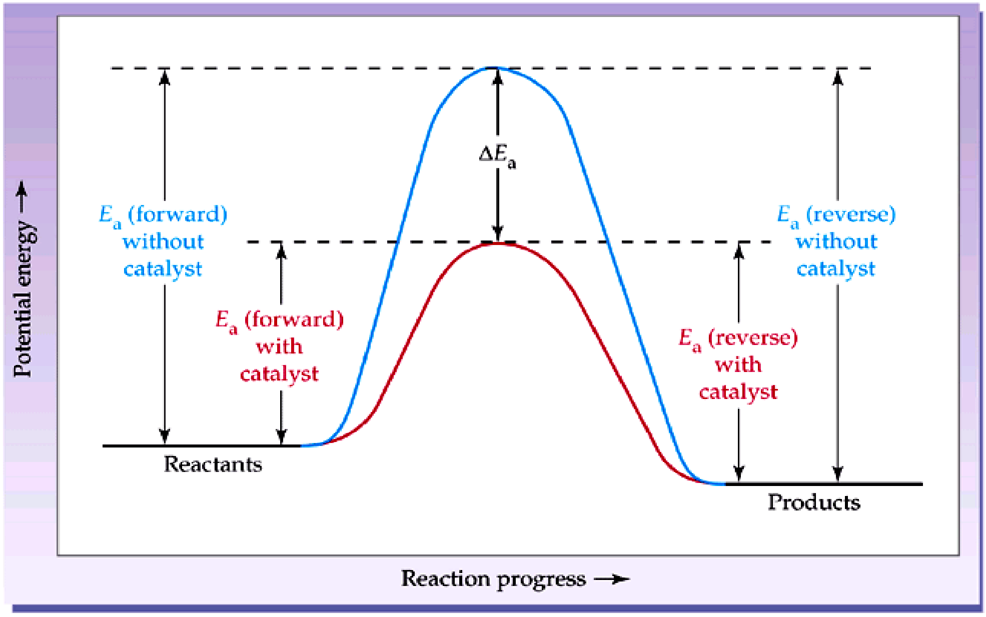


Figure 14.3 Effect of catalyst on reversible reaction

Kinetics of effect of catalyst in the position of chemical equilibrium

Let:

E_{afu} be activation energy for forward uncatalysed reaction

E_{abu} be activation energy for backward uncatalysed reaction

K_{cu} be equilibrium constant for uncatalysed reaction

K_{cc} be equilibrium constant for catalysed reaction

k_{fu} and k_{bu} be the rate constants for uncatalysed forward and backward reaction respectively

K_{fc} and K_{bc} be the rate constant for catalysed forward and backward reaction respectively

Then using: $K_c = \frac{k_f}{k_b}$

For uncatalysed reaction:

$$K_{cu} = \frac{k_{fu}}{k_{bu}}$$

But from Arrhenius equation $\left(k = Ae^{-E_a/RT}\right)$

$k_{fu} = Ae^{-E_{afu}/RT}$ and $k_{bu} = Ae^{-E_{abu}/RT}$

Then $K_{cu} = \frac{Ae^{-E_{afu}/RT}}{Ae^{-E_{abu}/RT}} = e^{\frac{E_{abu}}{RT} - \frac{E_{afu}}{RT}}$ (Apply division exponent rule)

Therefore $K_{cu} = e^{\frac{(E_{abu} - E_{afu})}{RT}}$

But $E_{afu} - E_{abu} = -(E_{afu} - E_{abu}) = -H_u$ (where H_u is the heat of uncatalysed reaction)

Hence $K_{cu} = e^{\frac{-H_u}{RT}}$

(Generally equilibrium constant (K_c) at temperature (T) is related to heat of reaction (H_r) by the following equation; $K_c = e^{\frac{-H_r}{RT}}$).

For catalysed reaction:

Similarly $K_{cc} = e^{-H_c/RT}$

Then finding the ratio of K_c values for catalysed and unanalyzed reaction

$\frac{K_{cu}}{K_{cc}} = \frac{e^{-H_u/RT}}{e^{-H_u/RT}} = e^{\left(\frac{H_c - H_u}{RT}\right)}$

But $H_c = H_u$ and therefore; $H_c - H_u = 0$

Thus $\frac{K_{cu}}{K_{cc}} = e^0 = 1$

Hence $K_{cu} = K_{cc}$

Conclusion

The catalyst does not change the value of equilibrium constant. It has no effect on the equilibrium constant value and the position of equilibrium as well.

Example 1

Sulphuric acid is manufactured by the contact process which makes use of the equilibrium reaction: $SO_2 + O_2 \rightleftharpoons 2SO_3$

Heat is given out in the formation of sulphur trioxide. State what effect there would be on the equilibrium concentration of sulphur trioxide if (i) the pressure were increased (ii) the temperature were raised.

Solution

(i) Concentration of sulphur trioxide will be increased (the forward reaction proceed with reduction of volume, thus increasing pressure will shift the position of equilibrium to the right and hence the production of SO_3 will be increased).

(ii) Concentration of sulphur trioxide will be decreased (since heat is given out; the forward reaction is exothermic so increase in temperature shifts position of equilibrium to the left and hence the production of SO_3 will be decreased).

Example 2

The equation for the reaction by which ammonia is manufactured is $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(a) What would be the effect on the equilibrium concentration of ammonia of
  (i) Increasing the pressure
  (ii) Increasing the nitrogen concentration
(b) The equilibrium concentration of ammonia increases as the temperature is lowered. Is heat evolved or absorbed when ammonia is formed?
(c) Why is a catalyst used in this reaction?

Solution

(a) (i) Concentration of ammonia will be increased

  (ii) Concentration of ammonia will be increased

(b) Heat is evolved (low temperature favours forward reaction of exothermic reaction)
(c) High percentage yield of ammonia is ensured by employing low temperature; but at low temperature the rate of the production of the gas is very slow and hence catalyst must be employed to increase the rate of production of the ammonia gas by enabling the equilibrium to be reached earlier.

Example 3

At 400°C, the three gases, hydrogen, iodine and hydrogen iodide exist together in equilibrium. The equation for the reaction is $H_2 + I_2 \rightleftharpoons 2HI$

What effect will an increase in pressure have on the position of equilibrium?

Solution

Increase in pressure has no effect on position of chemical equilibrium because the reaction does not accompany with change in volume of the reagents.

Example 4

The reaction $N_2 + O_2 \rightleftharpoons 2NO$ is reversible and (from left to right) endothermic, all reagents being gaseous. If the system is in equilibrium which (at temperature which allows quite rapid reaction), what if any, will be the effect on the equilibrium of

(a) Doubling the total pressure
(b) Doubling the pressure of nitrogen
(c) Lowering temperature slightly
(d) Explain briefly why this reaction (when used industrially) was not catalysed? What alternative was available?

Solution

(a) Has no effect
(b) *Position of chemical equilibrium will shift to right* because doubling the pressure of nitrogen gas, doubles its concentration so to lower the added concentration the equilibrium must shift to the right by producing more NO
(c) Position of equilibrium will shift to the left
(d) Since the forward reaction is endothermic, the production of NO (forward reaction) is favoured by high temperature which also increases the rate of production of NO at the same time. So industrially, they employ high temperature.

Example 5

Two solid allotropes A and B of densities 2.07 and 1.97gcm^{-3} respectively are in equilibrium according to $A(s) \rightleftharpoons 2B(s)\ \Delta H = +0.4\text{kJmol}^{-1}$

What is the effect of pressure in above equilibrium?

Solution

Has no effect because pressure has no effect in reaction whose reagents are in solid phase which are always uncompressible

Example 6

Consider the reaction: $X_2(g) + 3Y_2(g) \rightleftharpoons 2XY_3(g) \qquad \Delta H = -92\text{kJ/mol}$

Is the production of XY_3 favoured by low or large volume of the flask? Explain.

Solution

The production of the given gas is favoured by low volume of the flask: The reaction is accompanied with decrease of volume from the left to the right so the forward reaction (production of XY_3) is favoured by high pressure and from Boyle's law whereby pressure varies inversely proportional to the volume; high pressure is obtained when the volume of flask is low.

APPLICATION OF LE CHATELIER'S PRINCIPLE

Haber process

Haber process is the industrial manufacture of ammonia.

It uses the following reaction:

$$\begin{array}{llcll} N_2(g) + & 3H_2(g) & \rightleftharpoons & 2NH3(g) & \\ 1\text{vol} & 3\text{vol} & & 2\text{vol} & \Delta V = -2 \end{array}$$

The reaction (from left to right) is exothermic.

Effect of pressure

Ammonia is produced from its elements with significant reduction of volume of gases. Therefore, if the system is in equilibrium and the pressure is then raised, the equilibrium must shift so as to tend to lower the pressure (Le – Chatelier's principle). To do this, the volume must be reduced by production of more ammonia. That is **high pressure favours the production of ammonia.**

Effect of Temperature

The formation of ammonia from its elements is exothermic. If the system is in equilibrium and the temperature is then lowered, the equilibrium must shift so as to tend to raise the temperature again. That is, heat must be liberated by the production of more ammonia. That is **low temperature favour the production of ammonia**. *However, by lowering the temperature the rate of the reaction is reduced, that is larger amount of ammonia would be produced over very long time. So it is necessary to introduce a catalyst which give sufficient reaction rate in spite of a relatively low temperature.*

Effect of Concentration

If the system is in equilibrium and more nitrogen or hydrogen is then added to increase their concentration, Le Chatelier's principle requires the equilibrium to shift so as to tend to reduce the added concentration and this is done by the production of more ammonia. *However, this is not an economic, so does not applied in practice and there is no particular advantage in using excess of either material.*
The gases are used in the theoretical proportion of nitrogen to hydrogen, 1:3 by volume.
Conclusion
The conditions chosen in Haber process in accordance with the above discussion are:

- Very high pressure ($200-500\text{atm}$).
- Temperature of about 450°C.
- Catalyst: Finely divided reduced iron, usually 'promoted' by alumina (aluminium oxide).

Contact process

Contact process is the industrial manufacture of sulphuric acid. The first step in the contact process is the conversion of sulphur dioxide to sulphur trioxide according to the following reaction:

$$\begin{array}{llll} 2SO_2\,(g) + & O_2\,(g) & \rightleftharpoons & 2SO_3\,(g) \\ 2\text{vol} & 1\text{vol} & & 2\text{vol} \quad \Delta V = -1 \end{array}$$

The reaction (from left to right) is exothermic.

Effect of pressure

Sulphur trioxide is produced from its elements with small reduction of volume of gases. Therefore increasing in pressure of the system favours the production of SO_3 in smaller extent (compared to effect of pressure in production of ammonia where there is greater reduction of volume). *So as the construction of equipment for production of high pressure is very expensive, the application of high pressure in production of SO_3 is not an economic.*

Effect of temperature

The formation of SO_3 according to above reaction is exothermic. If the system is in equilibrium and the temperature is then lowered, the equilibrium must shift so as to tend to raise the temperature again. That is, heat must be liberated by production of more sulphur trioxide. Thus **low temperature favours the production of sulphur trioxide.** *However, by lowering temperature, the rate of the reaction is reduced, that is greater amount of sulphur trioxide would be produced but over very long time which is not an economic. So it is necessary to introduce a catalyst which will give sufficient reaction rate in spite of relatively low temperature.*

Effect of concentration

Suppose that in the contact process reaction, equilibrium has been reached in certain conditions and then the concentration of oxygen relative to sulphur dioxide is raised. Le Chatelier's principle requires the system to react to oppose this change and this is done by combining it with sulphur dioxide to form sulphur trioxide of sulphur trioxide. So **increase in concentration of oxygen (from air) favours the production of sulphur trioxide**. In practice, the sulphur dioxide and air mixture used contains about three times as much oxygen as is theoretically required for the sulphur dioxide content. Use of more air renders the product too dilute in sulphur dioxide. Also the use of high concentration sulphur dioxide relative to oxygen is not an economic (oxygen from air is cheaper than SO_2)
Conclusion
The conditions chosen in contact process in accordance with the above discussion are:

- Relatively low temperature of about 450°C
- High concentration of oxygen (relative to SO_2)
- Catalyst: Vanadium (v) oxide (V_2O_5)

DIGGING EXERCISE 14

EXERCISE 14A: BINDER QUESTIONS

Question 1

Given the hypothetical chemical reaction:

$$K_2 + N_2 \rightleftharpoons 2KN \quad \Delta H = -20.1Jmol^{-1}$$

Suggest the direction of equilibrium if:

(i) Pressure is decreased
(ii) Temperature is raised
(iii) K_2 is introduced in the system
(iv) N_2 is removed from the system
(v) KN is introduced in the system

Question 2

Consider the equilibrium: $N_2O_4(g) \rightleftharpoons 2NO_2(g) \;\; \Delta H^\theta = +58kJ/mol$

In which direction will equilibrium shift when?

(a) N_2O_4 is added
(b) NO_2 is removed
(c) The total pressure is increased by addition of $N_2(g)$
(d) The volume is increased.
(e) The temperature is decreased.

In each case give clear reason to support your answer.

Question 3

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6H_2(g) \rightleftharpoons 4PH_3(g) \;\; \Delta H = +110kJ/mol$$

Question 4

Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction $\left(K_c = \frac{K_f}{K_b}\right)$.

It is known that the magnitude of both rate constants are affected by catalyst. However, the catalyst is said to have no effect on the equilibrium constant; explain why.

Question 5

In which scenarios the following factors do not affect position of chemical equilibrium?

(i) Temperature
(ii) Concentration
(iii) Pressure
(iv) Catalyst

EXERCISE 14B: REAL QUESTIONS

Question 6

Explain why do we hear a hissing sound when we uncap a Coca Cola bottle?

Question 7

Explain conditions applied to increase the yield of ammonia in the Haber process indicating numerical values of pressure, temperature applied and also the kind of catalyst to be used.

Question 8

Quick lime is manufactured industrially by heating calcium carbonate in a lime kiln to a particular temperature that is not less than $800℃$. Inside the lime kiln, the carbonate undergoes thermal dissociation to produce the quick lime according to the following equation:

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

Explain why there is a constant pressure of carbon dioxide at the particular temperature and why a current air is blown through the lime kiln during production of quick lime.

Question 9

The manufacture of sulphuric acid is carried out on a large scale in most industrialised countries because it is needed by many other industries. In most countries the raw material is sulphur. The process consists of three main stages: the burning of sulphur in air, the conversion of sulphur dioxide to sulphur trioxide and the formation of sulphuric acid. The equation for the conversion to sulphur trioxide is;

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(i) The conversion to sulphur trioxide is favoured by low temperature. Is the reaction exothermic or endothermic? Explain.
(ii) Give the name of the catalyst used in this reaction. State the effect of the catalyst on the percentage yield at equilibrium of sulphur trioxide and on the rates of both forward and reverse reactions.
(iii) A typical operating temperature is 450 °C. State **one** advantage and **one** disadvantage of operating the process at a temperature $50℃$ lower.

Question 10

Haemoglobin (Hb) is the material in red blood cells responsible for transporting oxygen to the cells of human body. Each haemoglobin molecule carries four oxygen molecules in oxyhaemoglobin ($Hb(O_2)_4$), and the equilibrium conditions of the haemoglobin-oxygen interaction can be expressed as follows:

$$Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq)$$

For human to be healthy, sufficient oxygen in the air is needed so as to maintain healthy equilibrium.

(i) What does sufficient oxygen mean to the position of equilibrium of the above haemoglobin-oxygen interaction?
(ii) At very high altitude, a person tends to feel light-headed. Support this fact by using Le-Chatelier's principle.
(iii) For people born and raised at high altitudes their body produce more haemoglobin. Explain in terms of Le-Chatelier's principle, why this is important.

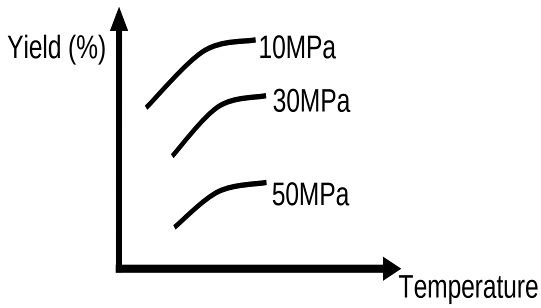
EXERCISE 14C: HOT QUESTIONS

Question 11

Does adding amount of a component in a system of chemical equilibrium always shift equilibrium position? Give an explanation to justify your answer.

Question 12

The diagram below shows the effect of temperature and pressure on the equilibrium yield of the product in a gaseous equilibrium.



(i) Use the diagram to deduce whether the forward reaction involves increase or decrease in the number of moles of gas. Explain your answer.
(ii) Use the diagram to deduce whether the forward reaction is exothermic or endothermic. Explain your answer.

Question 13

When bromine is dissolved in water, the following equilibrium is established:

$$\underset{\text{yellow}}{Br_2(aq)} + H_2O(l) \rightleftharpoons \underset{\text{colourless}}{H^+(aq) + Br^-(aq) + HBrO(aq)}$$

State and explain the effect on the colour of the solution of:

(a) Adding an acid
(b) Adding an alkali
(c) Adding solution of sodium bromide
(d) Adding a silver nitrate solution

Question 14

Apply Arrhenius equation, $k = Ae^{-E_a/RT}$ to the forward and backward reactions, and show that a catalyst increases the rates of both reactions by the same factor.

Question 15

Use the relation between the equilibrium constant and the forward and reverse rate constants, to show that a catalyst does not affect the value of the equilibrium constant.

EXAMINATION QUESTIONS FOR PART FOUR

Question 1

(a) Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction $\left(K_c = \frac{K_f}{K_b}\right)$. It is undeniable fact that the magnitude of both rate constants increases with an increase in temperature. However, for some reactions, magnitude of the equilibrium constant is found to decrease as the temperature increases; explain how is this possible?

(b) 2.00g of phosphorous pentachloride are allowed to reach equilibrium at 200°C in a vessel of $1dm^3$ capacity. If the equilibrium constant of the reaction: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 0.008 $moldm^{-3}$ at this temperature and in the conditions stated, calculate the percentage dissociation of the phosphorous pentachloride at equilibrium.

Question 2

The equilibrium constant, K_c, for the reaction of hydrogen with iodine is 57 at 700K and the reaction is endothermic.

$$H_2(g) \quad + \quad I_2(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \; 2HI(g); \quad K_c = 57 \text{ at } 700K$$

(a) Is the rate constant, K_f for the formation of HI larger or smaller than the rate constant, K_r for the decomposition of HI?

(b) The value of K_r at 700 is $1.16 \times 10^{-3}M^{-1}S^{-1}$. What is the value k_f at the same temperature?

(c) How are the values of k_f, k_r and K_c affected by the addition of a catalyst?

(d) How are the values of k_f, k_r and K_c affected by an increase in temperature?

Question 3

Nitrogen, hydrogen and oxygen undergo the reaction shown below:

Reaction 1: $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g) \qquad \Delta H_f^\theta = +91KJmol^{-1}$

Reaction 2: $\frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g) \rightleftharpoons NH_3(g) \qquad \Delta H_f^\theta = -46KJmol^{-1}$

Reaction 3: $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) \qquad \Delta H_f^\theta = -242KJmol^{-1}$

Use this information in answering the question below:

(a) In which, if any, of the reaction above would the percentage yield of products at equilibrium increase if the temperature were to be raised? Explain your answer.

(b) In which, if any, of the reactions above would the percentage yield of products at equilibrium not increase if the pressure were to be raised? Explain your answer.

(c)
 (i) In which direction, if any would any equilibrium reaction move if $\Delta H = 0$ and the temperature were to be decreased?
 (ii) Predict for which of the reactions above the percentage yield of products at equilibrium would be most affected by a change in temperature. Explain your answer.

Question 4

In the Haber process for manufacture of ammonia, nitrogen and hydrogen react as shown in the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \; \Delta H^\theta = -92kJ/mol$$

The table shows the percentage yield of ammonia, under different conditions of pressure and temperature when the reaction has reached dynamic equilibrium.

Temperature/ K	600	800	1000
% yield of ammonia at 10MPa	50	10	2
% yield of ammonia at 20MPa	60	16	4
%yield of ammonia at 50MPa	75	25	7

(a) Explain the meaning of the term **dynamic equilibrium**.

(b) Use Le-Chatelier's principle to explain why, at given temperature, the percentage yield of ammonia increases with an increase in overall pressure.
(c) Give reason why a high pressure of 50MPa is not normally used in the Haber process although it gives better yield?
(d) Many industrial ammonia plants operate at a **compromise temperature** of about 800K.
 (i) State and explain, by using Le-Chatelier's principle one advantage of using temperature lower than 800K
 (ii) State the major advantage of using a temperature higher than 800K
 (iii) Hence (from (i) and (ii) above) explain why 800K is referred as a **compromise temperature**.

Question 5

(a) On what factors, does the value of the equilibrium constant of reaction depend?
(b) At 1127K and 1atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon is 90.55% CO by mass:

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

Calculate K_c for this reaction at the above temperature.

Question 6

(a) What is meant by:
 (i) A chemical equilibrium
 (ii) The position of chemical equilibrium
(b) A 1:3 mixture by volume of nitrogen and hydrogen gases was made up and left to equilibrium at $1.01 \times 10^6 N/m^2$ at 327°C. Calculate equilibrium constant, K_p given that the equilibrium partial pressure of ammonia is 15%

Question 7

(a) In the preparation of ethylethanoate shown in the equation below, concentrated H_2SO_4 is often added to the mixture:

$$C_2H_5OH + CH_3COOH \xrightarrow[\text{conc.}H_2SO_4]{} CH_3COOC_2H_5 + H_2O$$

 (i) State two (2) functions of concentrated H_2SO_4 in the production of the compound.
 (ii) What will be the effect of adding $NaOH(aq)$ instead of conc. H_2SO_4 in the production of the compound?
(b)
 (i) When $1.00 mol/dm^3$ of CH_3COOH were heated with 0.18mol of C_2H_5OH in a $1dm^3$ closed vessel, 0.829mol of CH_3COOH remained at equilibrium. Calculate the value of K_c
 (ii) What mass of ethylethanoate should be present in the equilibrium mixture formed under the same experimental conditions as $9(b)(i)$ above if 0.30moles of ethanol were heated with 0.20moles of ethanoic acid in $1.0dm^3$ closed vessel?

Question 8

(a) Explain the meaning and significance of equilibrium constant.
(b) When the solution containing $[Ag^+] = 0.2M$ was added to the flask containing ferrous solution of 0.100M, Ferric of 0.3M and solid silver; ferrous convert silver ions to solid and itself it undergo oxidation. What are ions concentrations when the equilibrium is established? Given that; equilibrium constant for the reaction is 2.98.

Question 9

(a) Ammonia is manufactured by passing hot nitrogen at high pressure over on iron catalyst .The equation of the reaction for this process is given as: $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

The equilibrium constant for the reaction is expressed as:

$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$. Name and state the law applied to get the expression K_c

(b) If at 402°C, the reaction in (a) above has a K_p value of 2×10^{-14} Pa. calculate the pressure at which ammonia is 95% dissociated into its elements.
(c) What will happen to the value of K_p if 0.5 mole of NH_3 is added to the equilibrium mixture at 402°C

Question 10

(a) What does Van't Hoff's law of mobile say about the effect of temperature in the equilibrium position?
(b) At a certain high temperature, the equilibrium constant of the reaction:

$$N_2 + O_2 \rightleftharpoons 2NO \text{ is } 8 \times 10^{-4}$$

Assuming air to be a mixture of four volumes of nitrogen with one volume of oxygen, calculate the percentage of nitrogen monoxide by volume in the gas produced by allowing air to reach equilibrium at this temperature.

Question 11

(a) How does reaction quotient relate to equilibrium constant?
(b) At 817°C, K_p for the reaction between CO_2 and excess hot graphite to form $CO(g)$ is 10atm.
  (i) What is the mole fraction of each gas at equilibrium at 817°C and the total pressure of 4atm?
  (ii) At what total pressure, will the gas mixture contain 6% CO_2 by volume?

Question 12

(a) Consider the following reaction equations representing Haber process and contact process:

Haber process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92kJ/mol$

Contact process: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \ \Delta H = -196kJ/mol$

  (i) Which reaction whose equilibrium position is more affected by temperature? Give reason(s) for your answer.
  (ii) Which reaction whose equilibrium position is more affected by pressure? Give reason(s) for your answer.

(b) For the reaction: $A + B \rightleftharpoons 2C$; 2 moles of A and 3 moles of B reacts. If the equilibrium constant for the reaction, $K_c = 4$ at 900°C .What will be the equilibrium amount of C?

Question 13

(a) High pressure increases product yield of both Haber process and contact process. However unlike Haber process, contact process is carried out at just almost atmospheric pressure. Explain.
(b) At 250°C, K_p for the reaction: $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ is 8×10^{-4} . Nitrogen and oxygen gas are mixed in a volume ration of 4:1 respectively; calculate the percentage of nitric oxide by volume in the gas produced by allowing air to reach equilibrium at 250°C.

Question 14

(a) Write down two advantages of employing high pressure in the Haber process.
(b) At 25°C and 1atm pressure, the partial pressures in the equilibrium pressures of N_2O_4 and NO_2 gases are 0.7atm and 0.3atm respectively. Calculate the partial pressure of these gases when they are in the equilibrium at 25°C and at a total pressure of 10atm.

Question 15

(a) Which physical factor(s) affect the magnitude of equilibrium constant?
(b) How the factor(s) mentioned in (a) above, affect the magnitude of equilibrium constant?
(c) An equilibrium mixture at 300K contains N_2O_4 and NO_2 gases at 0.28atm and 1.1atm respectively; if the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.

Question 16

(a) Hydrogen chloride may be prepared by direct combination of hydrogen and chlorine as per the following reaction equation:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \ \Delta H = -184kJ/mol$$

What will be the effect on the percentage yield of HCl when:

  (i) The volume of reaction flask is halved.
  (ii) Temperature for the reaction is lowered.
  (iii) Concentration of both hydrogen and chlorine gas is doubled.

(b) At 250°C and 1atm of sulphur trioxide gas is 50% dissociated, calculate K_p and K_c for the reaction at 250°C

Question 17

(a) Ammonia is manufactured by the Haber process in which the following equilibrium is established.

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

(i) Why catalyst has no effect on position of this equilibrium?
(ii) At equilibrium, with a pressure of 35MPa and a temperature of $600K$, the yield of ammonia is 65%.

A: State why industry uses a temperature higher than $600K$.
B: State why industry uses a pressure lower than $35MPa$

(b) Calculate the numerical value of K_p for the decomposition of SO_2Cl_2, if its degree of dissociation under atmospheric pressure is 90%.

Question 18

(a) *Catalyst has no effect on chemical equilibrium.* What is wrong about this argument? Explain clearly.
(b) CO_2 dissociates according to; $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$.If under atmospheric pressure, 40% of CO_2 was dissociated; calculate the dissociation constant i.e K_p

Question 19

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

For the reaction above the rate constant at $380°C$ for the forward reaction is 2.6×10^3 L^2 $mol^{-2}s^{-1}$ and this reaction is first order in O_2 and second order in NO. The rate constant for the reverse reaction at 380°C is 4.1 $Lmol^{-1}s^{-1}$ and this reaction is second order in NO_2.

(a) Write the equilibrium expression for the reaction as indicated by the equation above and calculate the numerical value for the equilibrium constant at $380°C$.
(b) What is the rate of the production of NO_2 at $380°C$ if the concentration of NO is $0.006mol/L$ and the concentration of O_2 is $0.29mol/L$?
(c) The system above is studied at another temperature. A 0.2 mole sample of NO_2 is placed in a 5L container and allowed to come to equilibrium. When equilibrium is reached,15% of the original NO_2 has decomposed to NO and O_2. Calculate the value for the equilibrium constant at the second temperature.

Question 20

(a) What is each of the following principle/law doing?
(i) Le-Chatelier's principle
(ii) Law of mass action
(b) Dinitrogen tetraoxide in its liquid state was used as one of fuels on the Lunar lander expeditions for the NASA space vessels. In the gas phase it decomposes to gaseous nitrogen dioxide as shown in the following equation:

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

N_2O_4 was allowed to reach at equilibrium at $400°C$ where the value of $K_p = 0.133atm$. At equilibrium, the pressure of N_2O_4 was found to be 2.71atm.

(i) Write the equilibrium expression in terms of concentration.
(ii) Write the equilibrium expression in terms of partial pressures.
(iii) Calculate the equilibrium pressure of NO_2.

Question 21

(a) What do the following term represent?
(i) Reaction quotient
(ii) Equilibrium constant
(b) When 20.85g of PCl_5 was heated in a sealed tube of $4dm^3$ volume, the pressure in the vessel was found to be 1.5 atm. At this pressure it was found that PCl_5 dissociated to 80%. Calculate the partial pressure of each gas.

Question 22

(a) Consider the production of HI by direct combination between I_2 and H_2 as per question;

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Can you alter the yield of HI at equation by adding hydrogen gas or decreasing the volume of the container? Explain.

(b) Nitrogen and oxygen combine endothermically at elevated temperature according to the equation:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

If the equilibrium constant for the reaction is 4.3×10^{-3} at $3000°C$ and 1atm, calculate the composition of each in the equilibrium if 2 moles of each nitrogen and oxygen were heated.

Question 23

(a) Concentrated sulphuric acid reacts with sodium chloride as follows: $H_2SO_4 + Cl^- \rightleftharpoons HCl + HSO_4^-$
  (i) What would be observable result of this reaction?
  (ii) Explain why this reaction goes almost completely to the right despite the hydrochloric and sulphuric acids are strong.

(b) Given with the equilibrium for the following reactions:

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g) \quad K_c = 10^2$$
$$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = 10^3$$
$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 10^4$$

Calculate the equilibrium constant for the following reaction

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

Question 24

(a) What does the equilibrium law say and provide the corresponding equation.

(b) The following dynamic equilibrium was established at temperature T in a closed container.

$$P(g) + 2Q(g) \rightleftharpoons 2R(g); \ \Delta H^{\theta} = -50\ kJ/mol$$

The value of K_c for the reaction was $68.0 mol^{-1}dm^3$ when the equilibrium mixture contained 3.82mol of P and 5.24mol of R.

  (i) Write an expression of K_c for this reaction.
  (ii) The volume of container was $10dm^3$. Calculate the concentration in $moldm^{-3}$, of Q in the equilibrium mixture.
  (iii) State the effect, if any, on the equilibrium amount of P, and on the value of K_c of increasing the temperature.
  (iv) State the effect, if any, on the equilibrium amount of P, and on the value of K_c of using a container of larger volume.
  (v) Deduce the value of the equilibrium constant, at temperature T, for the reaction;

$$2R(g) \rightleftharpoons P(g) + 2Q(g)$$

Question 25

(a) The following equilibrium is established between colourless dinitrogen tetraoxide gas (N_2O_4) and dark brown nitrogen dioxide gas (NO_2).

$$N_2O_4(g) \rightleftharpoons 2NO_2(g); \ \Delta H = +58kJ/mol$$

  (i) Give two main features of reaction at equilibrium.
  (ii) Use Le Chatelier's principle to explain why the mixture of gases becomes darker in colour when the mixture is heated at constant pressure.
  (iii) Use Le Chatelier's principle to explain why the amount of NO_2 decreases when the pressure is increased at constant temperature.

(b) 24.4g of ethanoic acid and 24.3g of ethanol were mixed in stoppered bottle and left for several days to reach equilibrium at room temperature. At the end of that time, the mixture was poured into pure water and made up to a total volume of $250cm^3$. A $25.0cm^3$ sample of this needed $26.5cm^3$ of 0.400MNaOH to neutralise the remaining ethanoic acid. Calculate a value of K_c for the reaction:

$$CH_3COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3COOCH_2CH_3(l) + H_2O(l);$$

Question 26

(a) By referring to Le-Chatelier's principle and behaviour of particles; explain clearly two advantages of using high pressure in Haber process.

(b) A mixture was prepared using 1.00mol of propanoic acid, 2.00mol of ethanol and 5.00mol of water. At a given temperature, the mixture was left to reach equilibrium according to the following equation:

$$CH_3CH_2COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3CH_2COOCH_2CH_3(l) + H_2O(l); \Delta H = -22kJ/mol$$

The equilibrium mixture contained 0.54mol of the ester, ethyl propanoate.

(i) Write an expression for the equilibrium constant, K_c, for this equilibrium.
(ii) Calculate the number of moles of water in the equilibrium mixture.
(iii) Calculate a value for K_c for this equilibrium at this temperature. Why this K_c value has no units.
(iv) For this equilibrium, predict the effect of an increase in temperature on each of the following:

A: The amount of ester at equilibrium.
B: The time taken to reach equilibrium.
C: The value of K_c

Question 27

(a) When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an **equilibrium** is established. The organic product is a pleasant-smelling ester.

$$(CH_3)_2CHCH_2COOH + CH_3CH_2OH \rightleftharpoons \underset{\textbf{Ester}}{(CH_3)_2CHCH_2COOCH_2CH_3} + H_2O$$

The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than theoretical ratio of 1 to 1.

(i) By referring to the reaction between the 3-methylbutanoic acid and ethanol above; explain clearly the meaning of the term **equilibrium**.
(ii) Explain why 1 to 10 mole ratio is used and not the theoretical one. (You should **not** refer to cost).
(iii) Explain the effect of catalyst in the equilibrium.

(b) The equilibrium constant for the reaction;

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 986°C is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0atm.

(i) Calculate the number of moles of H_2 present at equilibrium.
(ii) Calculate the partial pressure of gases at equilibrium mixture.

Question 28

(a) For the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g), K_p = 794$ at 298K and $K_p = 54$ at 700K. Is the formation of HI favoured more at the higher or lower temperature? Give a reason for your answer.

(b) When a 0.218mol of hydrogen iodide was heated in a flask of volume Vdm^3, the following equilibrium was established at 700K. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

The equilibrium mixture was found to contain 0.023mol of hydrogen.

(i) Write an expression for K_c for the equilibrium
(ii) State why the volume of the flask need not be known when calculating a value of K_c
(iii) Calculate the value of K_c at 700K
(iv) Calculate the value of K_c for the equilibrium $H_2(g) + I_2 \rightleftharpoons 2HI(g)$

Question 29

(a) Three reactions, and their equilibrium constants, are gives below.

I. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 4.7 \times 10^{-31}$
II. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $K_c = 1.8 \times 10^{-6}$
III. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_c = 0.025$

Arrange above equations in order of their tendency to form products.

(b) Consider the gas-phase hydration of hexafluoroacetone, $(CF_3)_2CO$;

$$(CF_3)_2CO(g) + H_2O(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CF_3)_2C(OH)_2(g)$$

At 76°C , the forward and reverse rate constant are $K_f = 0.13M^{-1}s^{-1}$ and $K_r = 6.02 \times 10^{-4}s^{-1}$.

What is the value of the equilibrium constant, K_c?

(c) Consider the following heterogeneous equilibrium reaction: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

At 800°C, the pressure of CO_2 gas is 0.236 atm. Calculate: (i) K_p and (ii) K_c for the reaction at this temperature.

Question 30

(a) A platinum catalyst is used in automobile catalytic converter to hasten the oxidation of carbon monoxide:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad \Delta H^\theta = -566kJ/mol$$

Suppose that you have a reaction vessel containing an equilibrium mixture of CO (g), O_2(g) and CO_2(g). Under the following conditions, will the amount of CO increase, decrease, or remain the same?

(i) A platinum is added is added
(ii) The temperature is increased
(iii) The pressure is increased by decreasing the volume
(iv) The pressure is increased by adding argon gas
(v) The pressure is increased by adding O_2 gas.

(b) For the equilibrium: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; the equilibrium constant, K_p, has the value of 0.497 at 500K. A gas cylinder at 500K is charged with $PCl_5(g)$ at initial pressure of 1.66atm.What are equilibrium pressures of PCl_5, PCl_3 and Cl_2 at this temperature?

Question 31

At temperature near 800°C, steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2.

$$C\,(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called **water gas**.

(a) At 880°C, the equilibrium constant for this reaction is $K_p = 14.1$.What are the equilibrium partial pressures of H_2O,CO and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100mol of H_2O in a 1L vessel?
(b) What is the minimum amount of carbon required to achieve equilibrium under these conditions?

Question 32

(a) Listed in the table are forward and reverse rate constant for the reaction: $NO(g) \rightleftharpoons N_2(g) + O_2(g)$

Temperature (K)	$K_f(M^{-1}s^{-1})$	$K_r(M^{-1}s^{-1})$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic? Explain in the terms of kinetics.

(b) The equilibrium mixture, $SO_2 + NO_2 \rightleftharpoons SO_3 + NO$ was found to contain 0.6mol SO_3, 0.4mol of NO, 0.8mol of SO_2 and 0.1mol of NO_2 in a 1L vessel. One mole of NO was then forced into the reaction vessel with volume and temperature being constant. Calculate the amounts of each gas in the new equilibrium mixture.

Question 33

(a) When 1mol of PCl_5 is introduced into a 5L container at 500K, 78.5% of the PCl_5 dissociates to give an equilibrium mixture of PCl_5, PCl_3 and Cl_2.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g).$$

Calculate the value of K_p and K_c

(b) If the initial concentrations in a particular mixture of reactants and products (in (a) above) are $[PCl_5] = 0.5M$,$[PCl_3] = 0.15M$ and $[Cl_2] = 0.6M$;
   (i) In which direction does the reaction proceed to reach equilibrium?
   (ii) What are the concentrations when the mixture reaches equilibrium?

Question 34

(a) Suggest four ways in which concentration of hydrazine N_2H_4 could be increased in an equilibrium described by the equation:

   $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g);\ \ \Delta H = +95kJ/mol$

(b) PCl_5 dissociates according to the reaction;

   $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g); K_p = 1.78atm\ at\ 523K$

   Find the density of the equilibrium mixture at a total pressure of 1atm.

Question 35

(a) Consider the following reversible equilibrium:

$$2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(l)$$

Derive the relationship between K_c and K_p.

(b) At 90°C, the following equilibrium is established:

$$H_2(g) + S(s) \rightleftharpoons H_2S(g);\ \ K_p = 6.8 \times 10^{-2}$$

If 0.2mol of hydrogen and 1.0mol of sulphur are heated to 90°C, in a litre vessel; what will be partial pressure of H_2S at equilibrium?

Question 36

(a) Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction $\left(K_c = \frac{K_f}{K_b}\right)$. It is known that the magnitude of both rate constants increases with an increase in temperature. Explain why the K_c value changes as the result of the increase in temperature despite the fact that both K_f and K_b values are increased by the temperature rise.

(b) A 16g sample of sulphur trioxide was placed in an empty container where it decomposed at 800K according to the following chemical reaction:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

At equilibrium, the total pressure and the density of the gaseous mixture were 3.6atm and $3.2gdm^{-3}$ respectively. Calculate K_p for this reaction.

Question 37

(a) At a given temperature, the reaction quotient for a system at equilibrium is constant. Is this correct? Rationalise your answer.

(b) When 2.98 moles of I_2 and 8.10 moles of H_2 are heated at constant volume at 444°C until equilibrium, 5.64moles of HI are formed. If we start with 5.3 moles of I_2 and 7.94 moles of H_2, how much HI is present at equilibrium at the same temperature?

Question 38

(a) The expression for an equilibrium constant,K_c, for a homogeneous equilibrium reaction is given below.

$$K_c = \frac{[A]^3[B]^2}{[C]^4[D]^3}$$

   (i) Write an equation for the forward reaction.
   (ii) Deduce the units of K_c
   (iii) State what can be deduced from the fact that the value of K_c is larger when the equilibrium is established at a lower temperature.

(b) Consider the following reaction: $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$.

If nitrosyl bromine (NOBr) is 33.33% dissociated at 25°C and a total pressure is 0.28atm. Calculate K_p for the dissociation at this temperature.

Question 39

(a) The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

(b) Study the gases equilibrium: $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)\ \Delta H^\theta(g) = kJ/mol$
   (i) Write an expression for the equilibrium constant, K_p, in terms of partial pressure.
   (ii) At 60°C, 1.00dm ^{3} of the gas weighed 2.585g under a pressure of $1.01 \times 10^5 N/m^2$. Find the degree of dissociation of N_2O_4 and the value of K_p.

Question 40

(a) The following equation represents a reversible decomposition:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Under what condition(s) will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

(b) At 311K Sulphur dioxide and oxygen combine in equilibrium reaction according to the equation:

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

0.1mole of oxygen and 0.2 mole of sulphur dioxide are introduced into a 0.2L flask and were allowed to react. If the equilibrium amount of oxygen and sulphur dioxide is 10% of the equilibrium mixtures, calculate:

   (i) The equilibrium amount of oxygen, sulphur dioxide and sulphur trioxide
   (ii) Calculate the total pressure of the system at equilibrium

Question 41

(a) For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Comment on the magnitude of equilibrium constant(K_c) for this reaction?
(b) 23.8g of sulphur thiochloride ($SOCl_2$) were mixed with 19.2g of SO and 142g of Cl_2 in 1 dm^3 vessel at once and the reaction was allowed to establish equilibrium. Calculate the equilibrium composition of each gas if the equilibrium constant K_c for the reaction: $SOCl_{2(g)} \rightleftharpoons SO_{(g)} + Cl_{2(g)}$ is 1.2M.

Question 42

(a) What is the chemical equilibrium?
(b) What are necessary conditions for chemical equilibrium to be established?
(c) When one mole ethanoic acid (acetic acid) is maintained at 25°C with one mole of ethanol, one third of the ethanoic acid remains when equilibrium is attained. How much would have remained if three quarters of one mole of ethanol had been used instead of one mole at the same temperature?

Question 43

(a) Consider the following equilibrium: $\underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}} + 2H^+$

What would you expect to see if:

   (i) Dilute sodium hydroxide is added to the equilibrium mixture?
   (ii) Dilute hydrochloric acid is added to the equilibrium mixture?
   (iii) Calcium chloride is added to the equilibrium mixture?
(b) At 1 atmosphere, and 55°C N_2O_4 is 50% dissociated. Calculate the equilibrium constant for this reaction in terms of pressure. Hence calculate the degree of dissociation of the gas at 55°C and 10 atmosphere pressure.

Question 44

(a)
  - (i) Briefly explain the dynamic nature of equilibrium reaction.
  - (ii) Use hydrogen (H_2) and iodine (I_2) gases which produce hydrogen iodide (HI) gas to illustrate the point mentioned in (a)(i)

(b) At certain temperature, and a pressure of 1 atmosphere, iodine vapour contains 40% by volume of iodine atoms. $I_2 \rightleftharpoons I + I$. At what total pressure (without temperature change) would this pressure reduced to 20?

Question 45

(a) For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Comment on the value of equilibrium constant for the titration reaction.

(b) Nitrogen and oxygen combine at high temperatures with absorption of heat according to the equation:

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

The equilibrium constant for this reaction at 2680K and 1atm is 3.6×10^{-3} when equal volumes of nitrogen and oxygen are mixed at 2680K and 1atm and allowed to react until equilibrium is reached. Calculate the fraction

  - (i) Of the original nitrogen which is used in the reaction.
  - (ii) By volume of nitric oxide in the mixture.

Question 46

(a) Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal? Rationalise your answer.

(b) Pure phosphorous pentachloride gas is introduced into an evacuated vessel and comes to equilibrium at 250°C, the reaction being $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

The total pressure is 202kPa and the mole fraction of the chlorine gas is 0.407.

  - (i) What are the partial pressure of phosphorous trichloride and phosphorous pentachloride gases?
  - (ii) Calculate K_p for the reaction at 250°C.

Question 47

(a) In the course of a chemical reaction, when does a reaction quotient:
  - (i) Is zero?
  - (ii) Is infinitely large?

(b) At 700K, CO_2 and H_2 react to form CO and H_2O. For this process, K_c value is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated;
  - (i) Calculate the amount of each at equilibrium.
  - (ii) After equilibrium is reached another 0.34moles of CO_2 and 0.34 moles of H_2 are added to the reaction mixture. Find out the composition of the mixture of the new equilibrium state.

Question 48

(a) Given the following information:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g); K_p = 54 \text{ at } 700K$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); K_p = 1.04 \times 10^{-4} \text{at } 700K$$

Determine the value of K_p of the following reaction at 700K.

$$2NH_3(g) + 3I_2(g) \rightleftharpoons 6HI(g) + N_2(g)$$

(b) In a mixture of nitrogen gas and hydrogen gas at molar ratio of 1:3, the molar percent of NH_3 at equilibrium was found to be 1.2 at 500°C and 10atm
  - (i) Calculate K_p.
  - (ii) Find the pressure at which the equilibrium mixture at this temperature contain 10.4 molar percent?

Question 49

(a) Is a system at equilibrium if the concentrations of reactants and products are equal? Rationalise your answer.

(b) At 450°C, K_c for the equilibrium: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 1.8. How many moles of NH_3 must be placed in 1litre container in order to yield an equilibrium concentration of hydrogen gas of 6 moles per litre?

Question 50

(a) Why the equilibrium of decomposition of calcium carbonate to calcium oxide is not be achieved in the open container?

(b) A mixture of SO_3, SO_2 gas and O_2 gas is maintained in 10litre flask at 500°C for which K_c for the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ is 100.

  (i) If the moles of SO_2 and SO_3 are equal in the flask how many moles of O_2 are present?

  (ii) If the number of moles of SO_3 is twice the number of moles of SO_2, how many moles of O_2 present?

Question 51

(a) Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

(b) Consider the reaction:

$2HF(g) \rightleftharpoons H_2(g) + F_2(g) \quad \text{where } K_c = 1 \times 10^{-2}$

In an experiment, 5mol of $HF(g)$, 0.5mol of $H_2(g)$, and 0.75mol of $F_2(g)$ are mixed in a 5L flask and allowed to react to equilibrium, calculate concentrations of all species at equilibrium.

Question 52

(a) Equilibrium concentration depends on equilibrium constant. Explain whether you agree or disagree with this statement.

(b) Solid ammonium carbamate(NH_2COONH_4) dissociates as;

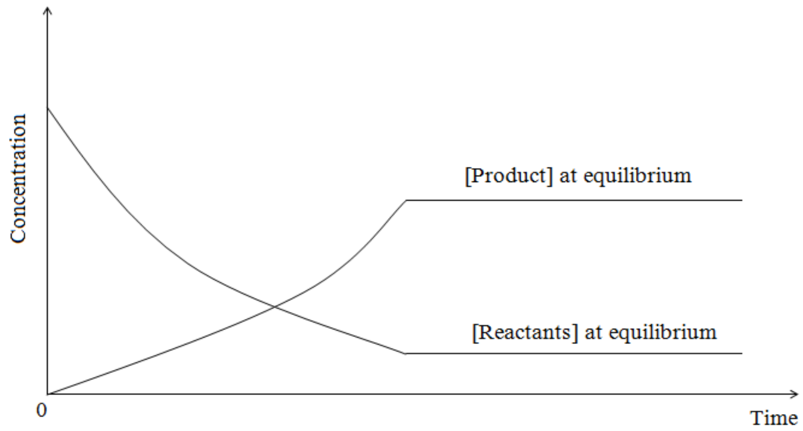
$$NH_2COONH_4 \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In a closed vessel, solid ammonium carbamate is in equilibrium with dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at equilibrium to that of original total pressure.

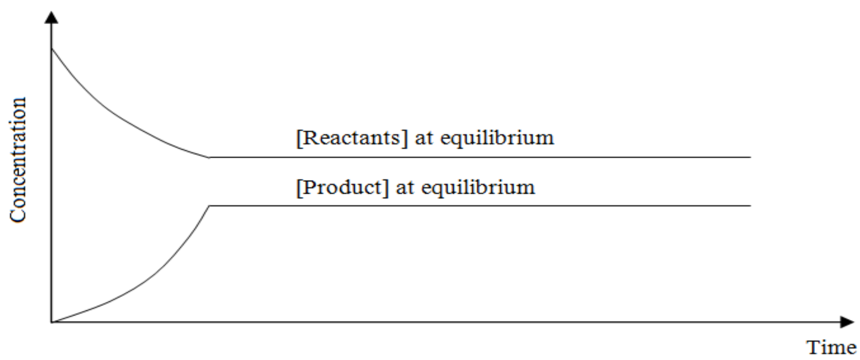
EXERCISE 13

1.

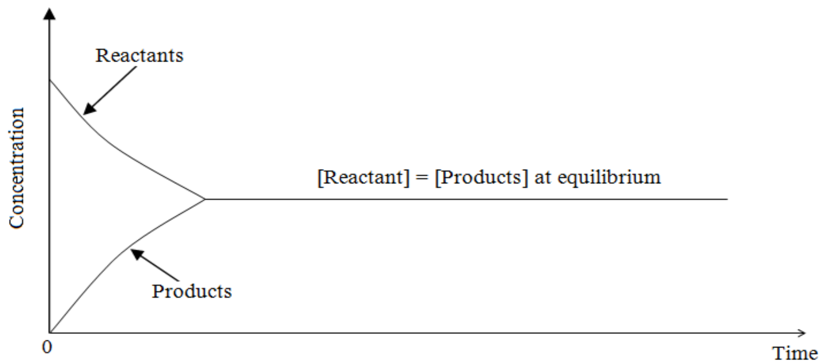
(a)



(b)



(c)



2. Only $H_2(g)$

3. Forward direction

Explanation

Greater rate of forward reaction, means that there is much high concentration of reactants. So it must proceed in forward direction to decrease the concentration and the rate of forward reaction as well till the equilibrium.

4. No.

Explanation

For the equilibrium to be established the reversible reaction must take place in a closed system. But in this case, the system is not closed as products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

5.

1) At equilibrium state, the rates of forward and backward reactions are equal.
2) The observable properties such as pressure, concentration, colour, density, viscosity etc., of the system remain unchanged with time once the system has attained chemical equilibrium.
3) The chemical equilibrium is a dynamic equilibrium because both the forward and backward reactions continue to occur even through it appears static externally.
4) The chemical equilibrium can be reached by starting the reaction either from the reactants side or from the product side.
5) Both pressure and concentration affect the position of equilibrium but do not affect the equilibrium constant.
6) The temperature can affect both the position of equilibrium as well as the equilibrium constant.
7) A positive catalyst can increase the rates of both forward and backward reactions and thus helping the system to attain the equilibrium faster; but it does not affect the position of equilibrium and equilibrium constant.

6.

(i) If the reaction has greater value of K_c then the reaction is more forward. Thus the first reaction is most forward followed by the second reaction while the third reaction having lowest value of K_c is most backward (least forward).
(ii) First reaction which involve combination of H_2 and Cl_2 to form HCl.

7. No; reactions with large equilibrium constant are not necessary to be very fast.

Reason:

Equilibrium constant is the measure of relative concentration of reactants and products at equilibrium. So even slow reactions with greater concentration of products than that of reactants have large equilibrium constants.

8. This is because, equilibrium constant is uniquely found by using concentration of reagents when the chemical system of the reversible reaction is at equilibrium and it is constant at given temperature while reaction quotient is found by using the concentrations at any time in the course of the reversible reaction and may take any value from 0 (with non-zero initial concentration of reactants and zero concentration of products) to infinitely large (with zero initial concentration of reactants and non-zero concentration of products).

9.

(a) $K_c = \frac{[CO]}{[CO_2][H_2]}$

(b) $K_c = \frac{[CO_2]^2}{[CO]^2}$

(c) $K_c = \frac{[Cr^{3+}]}{[Ag^+]^3}$

(d) $K_c = \frac{[H_2]^4}{[H_2O]^4}$

10.

(i) $K_p = \frac{(P_{N_2})(P_{H_2O})^2}{(P_{N_2H_4})(P_{O_2})}$

(ii) $K_p = \frac{(P_{H_2})^4}{(P_{H_2O})^4}$ or $K_p = \left(\frac{P_{H_2}}{P_{H_2O}}\right)^4$

(iii) $K_p = \frac{(P_{CO})}{(P_{CO_2})(P_{H_2})}$

(iv) $K_c = \frac{[Cr^{3+}]}{[Ag^+]^3}$

11. $[Ag(NH_3)_2]^+$ is more stable.

Reason: Large value of K_c implies that the position of equilibrium lies to the $[Ag(NH_3)_2]^+$ side (right hand side).

12.

(i) Capable of attaining equilibrium
Explanation:

$CaCO_3$ Decomposes, forming CaO(s) and CO_2(g) until the equilibrium pressure of CO_2 is attained (However there must be enough $CaCO_3$ to produce enough amount of CO_2 to exert equilibrium pressure).

(ii) Capable of attaining equilibrium
Explanation:

CO_2 continues to combine with CaO until the partial pressure of the CO_2 decrease to the equilibrium value.

(iii) Not capable of attaining equilibrium
Explanation:

There is no CaO present, so equilibrium cannot be attained because there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some of the CO_2 to react with CaO).

(iv) Capable of attaining equilibrium
Explanation:

$CaCO_3$ decomposes until the equilibrium pressure of CO_2 is attained.

13. $K_p = 2.3 \times 10^2 atm^2$

14. $K_c = \frac{[NO_2][O_2]}{[NO]^2}$; $K_c = \frac{[NO_2][O_2]}{[NO]^2} = \frac{1}{\frac{[NO]^2}{[NO_2][O_2]}} = \frac{1}{1\times10^{-30}} = 1 \times 10^{30}$

15.

(a) Essentially goes to completion
(b) Essentially not taking place(no reaction)
(c) Essentially goes to completion

16. $0.308\text{atm}\,(\text{or } 234\text{torr})$

17. $K_p = 0.113\text{atm}$

18. $K_c = 1.22\text{dm}^6\text{mol}^{-2}$

19. The equilibrium vapour pressure is $5 \times 10^{-15}\mathrm{atm}$.

20. The value of K_p is $0.0313\mathrm{atm}$; The value of K_c is $1.28 \times 10^{-3}\mathrm{mol/L}$

21.

1) An equilibrium between gaseous carbon dioxide and dissolved carbon dioxide inside the sealed soda drink.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

2) Interconversion between haemoglobin (Hb) and oxyhaemoglobin ($Hb(O_2)_4$) in the human body.

$$Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq)$$

22. Because undissolved carbon dioxide and dissolved carbon dioxide are in dynamic equilibrium; that is gaseous carbon dioxide is dissolving into the liquid form at the same rate that the liquid form of carbon dioxide is being converted back to its gaseous form. So there is a constant movement of CO_2 from the liquid to the gas phase and vice versa.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

23.

(i) After evaporation of liquid vapour in the closed container, the vapour formed undergoes condensation in the upper part of the container and lid as well. So the process of evaporation is reversible physical process. At the beginning of the evaporation process, there is no enough vapour to allow water vapour to condense at high rate and thus the rate of evaporation of the liquid will be greater than the rate of condensation of vapour. As the evaporation proceed, more vapour are formed and thus the rate of condensation increases until the rate of the condensation is equal to the rate of evaporation where the physical equilibrium between liquid water and gaseous water is said to be achieved.

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

(ii) Vapour pressure

Reasons:

1) They are both determined when the system achieve equilibrium.
2) They are both independent to the amount of their corresponding substances (vapour pressure does not depend upon the amount of liquid, in this case liquid water while equilibrium constant does not depend upon the amount of reactants and products).
3) They both temperature dependent.

(iii) They are similar in the following manner:

1) They are both need closed system to be formed.
2) They both have parameters that are constant with time.
3) They are both temperature and pressure dependent.

They are different in the following manner:

1) Physical equilibrium is achieved when physical state of the system does not change with time while chemical equilibrium is achieved when concentrations of reactants and products do not change with time.
2) Physical equilibrium shows no change in physical state of matter that is involved in the equilibrium while chemical equilibrium shows no change in concentration of reactants and products that are involved in the equilibrium.
3) Physical equilibrium includes coexistence of two physical states inside the same closed system while chemical equilibrium includes equal rate of forward and reverse reactions.

24.

(i) Haemoglobin-carbon monoxide bond is stronger.

Reason:

Higher equilibrium constant for the second reaction, forward reaction in the second reaction is more favoured than in the first reaction which in turn means $Hb(CO)_4$ is more stable than $Hb(O_2)_4$.

(ii) Carbon monoxide will be consumed more.

Reason:

Higher equilibrium constant for the second reaction, forward reaction in the second reaction is more favoured than in the first reaction which in turn means haemoglobin has higher affinity to carbon monoxide than oxygen.

25. By calculating K_p value from the answer she got (and other given data) and then comparing the calculated K_p value with the given K_p as follows:

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3}$$

Substituting; $1.45 \times 10^{-5} = \frac{\left(2.24\times10^{-2}\mathrm{atm}\right)^2}{0.432\mathrm{atm}\times(0.928\mathrm{atm})^3} = 1.45 \times 10^{-3} \neq 1.45 \times 10^{-5}$

Since the calculated K_p value is different the given K_p value, the answer was wrong.

26. By calculating K_c value from the answer she got (and other given data) and then comparing the calculated K_c value with the given K_c as follows:

The least amount of acetic acid which is one of the reactants, is found when the reaction is at equilibrium. Thus, the mass of 1.8g, is the mass of acetic acid that remained at the equilibrium.

Then at equilibrium: Number of moles acetic acid = $\frac{1.8\text{g}}{60\text{gmol}^{-1}} = 0.03\text{mol}$

Initially: Number of moles of acetic acid = $\frac{12\text{g}}{60\text{gmol}^{-1}} = 0.2\text{mol}$

Number of moles ethanol = $\frac{18.6\text{g}}{46\text{gmol}^{-1}} = 0.4\text{mol}$

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initially	0.2	0.4	0	0
At equilibrium	0.2 − x	0.4 − x	x	x

$$K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.2-x}{V}\right)\left(\frac{0.4-x}{V}\right)} = \frac{x^2}{x^2 - 0.6x + 0.08}$$

But at equilibrium, number of moles of CH_3COOH is 0.03mol

Then $0.2 - x = 0.03$ or $x = 0.17$

Then; $K_c = \frac{0.17^2}{0.17^2 - (0.6\times0.17) + 0.08} = 4.2 = \text{Given } K_c \text{ value}$

Since the calculated K_c value is equal to the given K_c value, the answer was correct.

27.

(i) Limestone undergoes thermal decomposition to give lime according to the following equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

From which; $K_p = P_{CO_2}$

Thus P_{CO_2} at 800°C was $1.16\text{atm} = K_p$

From ideal gas equilibrium; $n = \frac{PV}{RT}$

Thus maximum number of moles of CO_2 will be given by;

$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{1.16\times5}{0.082\times1073}$ or 0.0659mol (CO_2 is the product, so its amount at equilibrium, is the maximum amount of it which can be formed).

Thus mass of CO_2 which can be produced in the reaction under given condition cannot exceed 0.0659mol.

From the stoichiometric of the reaction, mole ratio of CO_2 to CaO (lime) is 1:1

Thus n_{CO_2}produced $= n_{CaO}$ produced= 0.0659mol

Thus number of moles of lime produced under given conditions, also cannot exceed 0.0659mol.

Using $m = nM_r$; mass of $CaO = 0.0659\text{mol} \times 56\text{g/mol}$ or 3.7g

So mass of the lime produced cannot exceed 3.7g which is below the target amount of 5g and hence the design was not successful.

(ii) No; the will not increase.

Reason: The solid limestone did not appear in the equilibrium constant expression (which implies that it has no effect in the equilibrium position) and hence adding its amount will not change the amount of lime produced.

(iii) Increase

Reason: From the formula of calculating number of moles of CO_2 $\left(n_{CO_2} = \frac{P_{CO_2}V}{RT}\right)$ which is equal to number of moles of lime, it can be deduced that number of moles of CO_2 and hence amount of the lime increases as the volume of the container increases.

Note:

The reason that has been provided in (iii) above agrees with Le-Chatelier's principle (we will study it later); that is, the increase in volume would decrease pressure (Boyle's law) and thus the equilibrium will shift to the lime side by producing more CO_2 which exerts more pressure to keep pressure constant despite the increase in volume of the container.

28.

(i) **If the amount of limestone is so small that it produces $CO_2(g)$ whose pressure is less than K_p value, no equilibrium will be achieved and the whole limestone will be converted to lime. This equilibrium-free situation, ends when the amount of limestone has been increased to the extent that it produces $CO_2(g)$ whose pressure is equal to K_p. So below that limit amount of limestone (which makes $P_{CO_2} = K_p$) no equilibrium will be achieved and the whole limestone will be converted to lime (no extra work will be needed to separate the two expected solids) while above the limit amount of limestone, equilibrium will be achieved and the extra work will be unavoidable. Hence, the required maximum amount of limestone will be obtained when the amount of limestone put in the vessel is equal to the amount (of limestone) required to produce the amount of $CO_2(g)$ whose pressure is equal to K_p.**

Now, limestone undergoes thermal decomposition to give lime according to the following equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

From which; $K_p = P_{CO_2}$

Thus P_{CO_2} at 800°C was $1.16atm = K_p$

From ideal gas equilibrium; $n = \frac{PV}{RT}$

Thus maximum number of moles of CO_2 will be given by;

$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{1.16\times10}{0.082\times1073}$ or 0.1318mol

Thus mass of CO_2 which can be produced in the reaction under given condition cannot exceed 0.1318mol

From the stoichiometric of the reaction, mole ratio of CO_2 to $CaCO_3$ (limestone) is 1:1 (n_{CO_2}produced $= n_{CaCO_3}$ reacted).

Thus number of moles of limestone reacted to produce that maximum amount of CO_2 was also 0.1318mol.

To avoid presence of any unreacted limestone, its number of moles that was put in the vessel must be also 0.1318mol.

Using $m = nM_r$; mass of $CaCO_3 = 0.1318mol \times 100g/mol$ or 13.18g

Hence maximum amount of the limestone is 13.18g

(ii) From the stoichiometric of the reaction, mole ratio of CO_2 to CaO (lime) is 1:1

Thus n_{CO_2}produced $= n_{CaO}$ produced= 0.1318mol

Using $m = nM_r$; mass of $CaO = 0.1318mol \times 56g/mol$ or 7.4g

Hence mass of the lime obtained was 7.4g.

Have you noticed?

Through doubling the volume of the container (from 5L to 10L), the target of preparing at least 5g of lime (in **question 6**) has now reached.

29. Because $Q_c > K_c$, the reverse reaction is more favoured.

30. No, not at equilibrium. Forward reaction occurs($Q_c < K_c$)

31. $[CO_2] = [H_2] = 0.69M; [H_2O] = [CO] = 0.31M$

32. $K_p = 0.338atm$

33.

(a) $P_{co} = P_{H_2} = 6.13atm, P_{H_2O} = 2.67atm$
(b) 0.8364g
(c) 14.93atm

Hint for part (b)

Find number of moles of $H_2O(g)$ reacted before reaching the equilibrium (You will get 0.0697mol).

Then from stoichiometric ratio of the given reaction equation find the corresponding number of moles of carbon required to react with this amount of $H_2O(g)$ which is actually minimum number of moles of carbon required to form the equilibrium because for the equilibrium to be established $H_2O(g)$ has to react with the carbon. Finally convert the number of moles of carbon (You will get also 0.0697mol) to mass by using $m = nMr$ to get 0.8364g.

Hint for part (c)

Simply find the sum of equilibrium partial pressure of each gas to get 14.93

(That is $6.13atm + 6.13atm + 2.67atm = 14.93$)

34. The value of K_p is 0.82atm

35. The partial pressure of CS_2 changes to the maximum, its value is 1.28atm

The partial pressure of S_2 changes to the minimum, its value is 0.14atm

36. Mass of C in 100g of gases = 13.71g

Number of moles of C atoms in $CS_2 = \frac{13.71g}{12gmol^{-1}} = 1.14mol$

But 1mol of CS_2 contains 1mol of C; so number of moles of CS_2 is also 0.18mol

Also 1mol of CS_2 contains 2mol of S atoms; so number of moles of S atoms in $CS_2 = 2 \times 1.14\text{mol} = 2.28\text{mol}$

Mass of S in 100g of gases $= 86.29\text{g}$

Total number of moles of S atoms $= \dfrac{86.29\text{g}}{32\text{gmol}^{-1}} = 2.7\text{mol}$

Number of moles of S atoms in S_2

$=$ Total number of moles of S atoms $-$ Number of moles of S atoms in CS_2

$= (2.7 - 2.28)\text{mol} = 0.42\text{mol}$

Number of moles of S_2 molecules $= \dfrac{0.42\text{mol}}{2} = 0.21\text{mol}$

Then from $C(s) + S_2(g) \rightleftharpoons CS_2(g)$;

$$K_c = \frac{[n_{CS_2}]}{[n_{S_2}]} = \frac{\frac{n_{CS_2}}{V}}{\frac{n_{S_2}}{V}} = \frac{n_{CS_2}}{n_{S_2}} = \frac{1.14\text{mol}}{0.21\text{mol}} = 5.4$$

37. The ratio of [NO] to $[NO_2]$ is 583: 5000

38. Number of moles of HI = 1.9 moles, Number of moles of $H_2 = 0.05$ moles, Number of moles of $I_2 = 1.15$ moles

39. The pressure of hydrogen is 96695Nm^{-2}**;** The pressure of steam is 4605Nm^{-2}

40. From the given reaction equation: $K_c = \frac{[CO][H_2O]}{[CO_2][H_2]}$

Then $K_c = \dfrac{\left(\frac{n_{CO}}{V}\right)\left(\frac{n_{H_2O}}{V}\right)}{\left(\frac{n_{CO_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)} = \dfrac{n_{CO} \times n_{H_2O}}{n_{CO_2} \times n_{H_2}}$

But for gases; mole ratio = volume ratio (from Avogadro's law)

Then: $K_c = \dfrac{V_{CO} \times V_{H_2O}}{V_{CO_2} \times V_{H_2}}$

Where V is the volume of each gas at equilibrium.

(a)	CO_2 +	$H_2 \rightleftharpoons$	CO +	H_2O
Initially	50	50	0	0
At equilibrium	$50 - x$	$50 - x$	x	x

Then $1.6 = \frac{x^2}{(50-x)^2} = \frac{x^2}{x^2-100x+2500} = 1.6 \quad x = 27.9$

Total volume of gaseous mixture

$= (50 - x) + (50 - x) + x + x = 100\text{cm}^3$

Hence:

The percentage of $CO = x = 27.9\%$

The percentage of $H_2O = x = 27.9\%$

The percentage of $H_2 = 50 - x = 22.1\%$

The percentage of $CO_2 = 50 - x = 22.1\%$

(b)	CO_2 +	$H_2 \rightleftharpoons$	CO +	H_2O
Initially	25	50	25	0
At equilibrium	$25 - x$	$50 - x$	$25 + x$	x

$$1.6 = \frac{x(25+)}{(25-x)(50-x)} = \frac{x^2 + 25x}{x^2 - 75x + 1250}$$

$0.6x^2 - 145x + 2000 = 0$ or $x = 14.68$

Total volume of gaseous mixture at equilibrium is;

$(25 - x) + (50 - x) + (25 + x) + x = 100\text{cm}^3$

Hence:

The percentage of CO_2 is 10.32%

The percentage of H_2 is 35.32%

The percentage of CO is 39.68%

The percentage of H_2O is 14.68%

It should be understood that:

In above equilibrium constant expression, water is included in the expression although its normal physical state is liquid while normal physical state of other reactants are gases because the reaction is undertaken at 1000°C where water exists in gaseous state as a vapour (steam).

41. The value of K_P is 50, the amount of I_2 remain unreacted is 0.11moles.

42. $[H_2] = 0.316M$, $[I_2] = 1.316M$, $[HI] = 4.368M$

43. Degree of dissociation of PCl_5 is 85%, K_P for the reaction is 2.6atm, K_c for the reaction is $0.06 mol/dm^3$.

44. Percentage of dissociation of H_2S is 1.28%

45. Given that:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ K_{P_1} = 3.1 \times 10^{-4} \ldots\ldots\ldots\ldots(1)$

$NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(g);\ K_{P_2} = 8.3 \times 10^{-3} \ldots\ldots\ldots(2)$

(i) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g);\ K_p = \frac{1}{K_{P_2}}$

So K_p for the (i) above $= \frac{1}{8.3\times10^{-3}atm^{-1}} = 1.2 \times 10^2 atm$

(ii) Taking $2 \times (2)$gives;

$2NH_3(g) + 2H_2S(g) \rightleftharpoons 2NH_4HS;\ K_{P_3} = (K_{P_2})^2 = 6.889 \times 10^{-5} \ldots(3)$

Then taking (1) + (3) gives

$N_2(g) + 3H_2(g) + 2NH_3(g) + 2H_2s(g) \rightleftharpoons 2NH_4HS(g) + 2NH_3;\ K_p = K_{P_1} \times K_{P_3}$

Or $N_2(g) + 3H_2(g) + 2H_2s(g) \rightleftharpoons 2NH_4Hs(g);\ K_p = (3.1 \times 10^{-4}atm^{-2})(6.889 \times 10^{-5}\ atm^{-2})$

$= 2.13559 \times 10^{-8}atm^{-4}$

Hence the K_p value for the reaction (ii) is $2.13559 \times 10^{-8}atm^{-4}$

EXERCISE 14

1.

(i) No effect on position of the chemical equilibrium.
(ii) The position of equilibrium will shift to the left.
(iii) The position of the equilibrium will shift to the right.
(iv) The position of the equilibrium will shift to the left.
(v) The position of the equilibrium will shift to the left.

2.

(a) The equilibrium shifts to the right.

Reason
The system will adjust to decrease the concentration of the added N_2O_4 by shifting to the NO_2 side.

(b) The equilibrium shifts to the right.

Reason
The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2.

(c) No shift to the position of the equilibrium.

Reason
Although adding N_2 will increase the total pressure of the system, N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 are therefore unchanged and hence there is no shift to the position of the equilibrium.

(d) The equilibrium shifts to the right.

Reason
If the volume is increase, the pressure of the system is decreased in accordance to Boyle's law and therefore the equilibrium will shift in the direction that has more gas molecules.

(e) The equilibrium shifts to the left.

Reason
The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the question. Decreasing the temperature, will shift the equilibrium in the direction that produces heat, that is in the N_2O_4 side.

3.

1) Adding amount of P_4
2) Adding amount of H_2
3) Increasing temperature
4) Increasing pressure

4. Catalyst lowers the activation energy of both forward reaction and backward reaction by the same magnitude. This makes K_f and K_b to increase by the same proportion and hence the K_c value remains unchanged.

5.

(i) When a reaction has (almost) zero heat of the reaction.
(ii) No scenario.
(iii) **First scenario:** When the reaction does not involve gas.

Second scenario: When reaction (even if it is involving gases) is not accompanied with change of number of gas particles.

(iv) Any scenario.

6. In the coca cola soda, carbon dioxide is dissolved at high pressure and form the following equilibrium:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Opening the bottle decreases the pressure in the bottle, shifts the equilibrium position to $CO_2(g)$ side, thereby the solubility of the gas is decreased and hence gas bubbles are suddenly escaping the bottle with the hissing sound.

7. In the Haber process, ammonia is produced as per equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ \Delta H = \text{negative}$$

The following conditions are applied to increase the yield of ammonia:

1) Very high pressure in the range of 200atm to 500atm

This shifts the position of equilibrium to the ammonia side (right hand side) as the production of ammonia per above equation is accompanied with significant reduction of volume.

2) Relative low temperature of 450℃.

The reaction is exothermic. So applying low temperature shifts the position of equilibrium to the ammonia side. However below 400℃ no ammonia is produced.

3) Catalyst based on finely divided reduced iron promoted by alumina.

The low temperature favours production of ammonia but at very slow rate. So it is necessary to introduce catalyst which gives sufficient reaction rate in spite of relatively low temperature.

8.

- Once equilibrium has been attained the concentration of carbon dioxide gas (CO_2) remain unchanged and hence the pressure become constant.
- The current of blown air displace $CO_2(g)$ from the line kiln thus removing the carbon dioxide and hence the position of chemical equilibrium will shift to the right by producing more quick lime.

9.

(i) Exothermic

Explanation

If the temperature is lowered the system must respond in accordance to Le-Chatelier's principle by producing heat (exothermic process) to compensate the amount of the heat lowered. Since the low temperature also favour the formation of sulphur trioxide, the conversion must be exothermic too.

(ii) **Name:** Vanadium(V) oxide.

Effect on the yield: No effect.

Effect on the rate: It increases the rate of both forward and backward reaction by equal amount.

(iii) **Advantage:** High yield of sulphur trioxide is obtained.

Disadvantage: Slow rate of producing sulphur trioxide.

10.

(i) Sufficient oxygen shifts equilibrium position to the oxyhaemoglobin side by producing more oxyhaemoglobin.
(ii) At high altitude the air pressure is lowered and the decrease in pressure shifts equilibrium position to the free oxygen side by producing more oxygen gas in accordance with Le-Chatelier's principle. This decreases the amount of oxyhaemoglobin and hence the person feels bad.
(iii) According to Le-Chatelier's principle, more haemoglobin means the position of equilibrium will shift to the oxyhaemoglobin side by producing more oxyhaemoglobin. This will ensure sufficient amount of oxyhaemoglobin in the body despite the decrease in the air pressure at high altitudes.

11. No.

Explanation:

Adding the amount of certain component in the chemical equilibrium will only shift the equilibrium position if it either changes concentration of reagents present in the equilibrium or changes their partial pressures.

Adding pure liquid or solid in the chemical equilibrium does not change the equilibrium position because they neither change the concentration nor appear in the equilibrium constant expression.

Also adding a gas like noble gas which does not react with gases (reagents) present in the equilibrium does not shift equilibrium position because the gas does not affect partial pressures of gases present in the equilibrium.

12.

(i) Increase

Explanation:

Low pressure gives higher yield.

(ii) Endothermic

Explanation:

Increase in temperature at given pressure increases the yield.

13.

(a) The solution will be yellow because addition of acid increase concentration of H^+ thus shifting the position of equilibrium to the left.
(b) The solution will be colourless because the alkaline solution neutralises an acid which is equivalent to removal of H^+ and hence the equilibrium will shift to right.
(c) The solution will be yellow because NaBr being strong ionic salt ionises completely yielding Br^-; so there is an increase in concentration of Br^-, the factor which shifts the position of chemical equilibrium to left.
(d) The solution will be colourless because the silver nitrate solution reacts with Br^- to give AgBr thus decreasing the concentration of Br^- and hence equilibrium shifts to the right.

14. Let:

E_{afu} and E_{abu} be activation energy for uncatalysed forward and backward reaction respectively.

E_{afc} and E_{abc} be activation energy for catalysed forward and backward reaction respectively.

K_{fu} and K_{bu} be the rate constants for uncatalysed forward and backward reaction respectively.

K_{fc} and K_{bc} be the rate constant for catalysed forward and backward reaction respectively.

For uncatalysed reaction:

From Arrhenius equation; $\left(K = Ae^{-E_a/RT}\right)$

$K_{fu} = Ae^{-E_{afu}/RT}$ and $K_{bu} = Ae^{-E_{abu}/RT}$

For catalysed reaction:

From the Arrhenius equation;

$K_{fc} = Ae^{-E_{afc}/RT}$ and $K_{bc} = Ae^{-E_{abc}/RT}$

Then, the increasing factor for forward reaction rate;

$$\frac{R_{catalysed}}{R_{uncatlysed}} = \frac{K_{fc}}{K_{fu}} = \frac{Ae^{-E_{afc}/RT}}{Ae^{-E_{afu}/RT}} = e^{\frac{E_{afu}-E_{afc}}{RT}}$$

And the increasing factor for backward reaction rate;

$$\frac{R_{catalysed}}{R_{uncatlysed}} = \frac{K_{bc}}{K_{bu}} = \frac{Ae^{-E_{abc}/RT}}{Ae^{-E_{abu}/RT}} = e^{\frac{E_{abu}-E_{abc}}{RT}}$$

But;

$E_{afu} - E_{afc} = E_{abu} - E_{abc} = \Delta E_a$

Thus;

The forward reaction factor $=$ The backward reaction factor $= e^{\frac{\Delta E_a}{RT}}$

Hence the catalyst increases the rates of both forward and backward reactions by the same factor.

15. Let: K_{cu} and K_{cc} be equilibrium constant for uncatalysed and catalysed reaction respectively.

Then using;

$$K_c = \frac{K_f}{K_b} = \frac{Ae^{-E_{af}/RT}}{Ae^{-E_{ab}/RT}} = e^{\frac{-(E_{af}-E_{ab})}{RT}}$$

But; $-(E_{af} - E_{ab}) = -\Delta H$; where ΔH is the heat of reaction

Thus; $K_c = e^{\frac{-\Delta H}{RT}}$

For uncatalysed reaction; $K_{cu} = e^{\frac{-H_u}{RT}}$

For catalysed reaction; $K_{cc} = e^{-H_c/RT}$

Then finding the ratio of K_c values for catalysed and uncatalysed reaction

$$\frac{K_{cu}}{K_{cc}} = \frac{e^{-H_u/RT}}{e^{-H_u/RT}} = e^{\left(\frac{H_c - H_u}{RT}\right)}$$

But $H_c = H_u$ and therefore; $H_c - H_u = 0$

Thus; $\frac{K_{cu}}{K_{cc}} = e^0 = 1$

Hence $K_{cu} = K_{cc}$ (catalyst does not change value of equilibrium constant).

SOLUTIONS TO EXAMINATION QUESTIONS

Question 1

(a) According to Arrhenius equation $\left(k = Ae^{\frac{-E_a}{RT}}\right)$; an increase in magnitude of rate constant at given temperature rise becomes high as the activation energy (E_a) becomes high too. For exothermic reactions, the activation energy of backward reaction is higher than that of forward reaction making the increase in K_b value greater than that of K_f value at the given temperature rise and hence the K_c value decreases as the temperature increases.

(b) Initially: Number of moles of $PCl_5 = \frac{2}{208.5}\text{mol} = 0.00959\text{mol}$

Equation for the reaction: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

At equilibrium $0.00959 - x \quad x \quad x$

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{0.00959 - x}{v}\right)} = \frac{x^2}{(0.00959 - x)v}$$

$x^2 + 0.008x - 0.00007672 = 0$ or $x = 0.005629$

Degree of dissociation of PCl_5:

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}}$$

$$= \frac{0.005629}{0.00959} = 0.587 \text{ or } 58.7\%$$

Hence degree of dissociation of PCl_5 is 58.7%

Question 2

(a) Because $K_c = \frac{k_f}{k_r} = 57$, the rate constant for the formation of HI (forward reaction) is larger than the rate constant for the decomposition of HI (reverse reaction) by a factor of 57.

(b) $K_c = \frac{k_f}{k_r}$

Substituting; $57 = \frac{k_f}{1.16 \times 10^{-3}M^{-1}S^{-1}}$

From which $K_f = 6.61 \times 10^{-2}M^{-1}s^{-1}$

(c) A catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount, thus increasing the rate constants k_f and k_r by the same factor. Because equilibrium constant, K_c equals to the ratio of k_f to k_r the value of K_c is unaffected by addition of catalyst.

(d) Because the reaction is endothermic, the activation energy for the forward reaction is greater than activation energy for the reverse reaction. Consequently, as the temperature increases, k_f increases more than k_r, and therefore $K_c = \frac{K_f}{K_r}$ increases, consistent with Le – Chatelier's principle.

Question 3

(a) Reaction 1

Explanation

The forward reaction is endothermic. So according to Le-Chatelier's principle, increase in temperature (which in turn increases heat at initial stage) will shift the position of equilibrium to the right hand side so as to absorb the added heat energy.

(b) Reaction 1

Explanation

The reaction is not accompanied with change in number of moles of gas molecules which in turn means the reaction does neither increase nor decrease the pressure and hence pressure has no effect on the equilibrium.

(c)
  (i) None
  (ii) Reaction 3

Explanation

The reaction has greatest enthalpy change and hence more affected with the change in temperature

Question 4

(a) It is the balance of the rate of the two reactions (forward and reverse reaction) which are proceeding at the same time in opposite directions. It is an equilibrium involving the constant interchange of particles in motion in opposite directions of forward and reverse reaction.

(b) System of chemical equilibrium opposes the change. So increase in pressure shifts the position of chemical equilibrium to the side with fewer moles (NH_3 – side) so as to decrease the pressure.

(c) Too expensive to generate such high pressure (50MPa) and therefore is not economic.

(d)

(i) Yield of ammonia increases

Explanation

The forward reaction is exothermic. So according to the Le-Chatelier's principle, the decrease in temperature will shift the position of equilibrium to the NH_3 − side so as increase the temperature.

(ii) Increase the rate of producing NH_3.

(iii) Balance between **rate** of producing NH_3 and **yield** of NH_3 (This means good yield of NH_3 is obtained at reasonable rate).

Question 5

(a) Depends on temperature only.

(b) Mass of CO in 100g of the mixture = 90.55g

Thus mass of CO_2 in the gaseous mixture = (100 – 90.55) g = 9.45g

Number of moles of CO $= \frac{90.55}{28}\text{mol} = 3.24\text{mol}$

Number of moles of CO_2 $= \frac{9.45}{44}\text{mol} = 0.215\text{mol}$

$$P_{co} = X_{co}P_T;\quad P_{CO} = \left(\frac{3.234}{3.234 + 0.215}\right) \times 1\text{atm} = 0.94\text{ atm}$$

$P_{CO_2} = P_T - P_{CO}$ (From Dalton's law of partial pressure)

$P_{CO_2} = (1 - 0.94)$ atm = 0 .06atm

Then $K_p = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(0.94\text{atm})^2}{0.06\text{atm}} = 14.73\text{atm}$

Using $\quad K_c = K_p(RT)^{m-n}$

Where:

m is the number of molecules in the reactant side = 1 (for gases only).

n is the number of molecules in the product side = 2.

Then; $K_c = 14.73 \times (0.082 \times 1127)^{1-2}\text{moldm}^{-3} = 0.159\text{moldm}^{-3}$

Hence the equilibrium constant, $K_c = 0.159\text{moldm}^{-3}$

Question 6

(a)

(i) Is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction.

(ii) Is the direction to which the reversible reaction proceeds so as to establish the equilibrium and therefore acting as the measure of relative concentrations of reacting substances at equilibrium.

(b)	$N_{2(g)} +$	$H_{2(g)} \rightleftharpoons$	$2NH_{3(g)}$
Initially (t = 0)	1	3	0
At equilibrium	$1 - x$	$3 - 3x$	$2x$

And total number of moles of gases at equilibrium,

$n_T = (1 - x) + (3 - 3x) + 2x = (4 - 2x)\text{moles}$

But from Avogadro's law; Mole ratio = volume ratio

Thus; percentage by volume of the gas = percentage by moles

Then $\left(\frac{n_{NH_3}}{n_T}\right) = 0.15$ or $\frac{2x}{4-2x} = 0.15$ or $x = 0.26$

$X_{H_2} = \frac{3-(3\times0.26)}{4-(2\times0.26)} = 0.64$

$X_{N_2} = \frac{1-0.26}{4-(2\times0.26)} = 0.21$

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(X_{NH_3}P_T)^2}{(X_{N_2}P_T)(X_{H_2}P_T)^3} = \frac{(X_{NH_3})^2}{(X_{N_2})(X_{H_2})^3P_T^2}$$

$$K_P = \frac{(0.15)^2}{0.21 \times (0.64)^3(1.01 \times 10^6)^2} = 4 \times 10^{-13}\text{Pa}^{-2}$$

Hence the equilibrium constant, K_p is $4 \times 10^{-13}\text{Pa}^{-2}$

Question 7

(a)

(i)

- Catalyses the reaction thus increasing the rate of production of the compound.
- Dehydrate (remove) water which makes the reaction to be more forward thus increasing percentage yield of the compound (ethylethanoate).

(ii) No significant production of ethylethanoate will be observed (Alkaline solution like NaOH is good catalyst for reverse reaction in the production of carboxylic acid like ethanoic acid).

(b) (i) $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	H_2O
Initially	0.18	1	0	0
At equilibrium	$0.18 - x$	$1 - x$	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.18-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{(0.18-x)(1-x)}$$

But $1 - x = 0.829$ (0.829 moles of CH_3COOH remained at equilibrium)

$x = 0.171$ moles

$$K_c = \frac{0.171^2}{(0.18 - 0.171)(1 - 0.171)} = 3.919$$

Hence the value of K_c is 3.919

(ii) $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	H_2O
Initially	0.3	0.2	0	0
At equilibrium	0.3 – x	$0.2 - x$	x	x

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.3-x}{V}\right)\left(\frac{0.2-x}{V}\right)} = \frac{x^2}{(0.3-x)(0.2-x)} = 3.919$$

$x^2 = 3.919x^2 - 1.9595x + 0.23514$

$x = 0.156$ moles ($x = 0.515$ is not practical solution because it exceeds initial amount of reactants present in the system).

Hence number of moles of ethylethanoate ($CH_3COOC_2H_5$) formed in a dm^3 was 0.156moles.

But molar mass of ethylethanoate = 88g /mole using $m = nM_r$

Mass of the ethylethanoate $= 0.156 \times 88g = 13.728g$

Hence mass of ethylethanoate in 1dm^3 of equilibrium mixture is 13.728g

Question 8

(a) This is the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients.

It is the fixed ratio which is obtained according to the equilibrium law.

For the reaction: $Aa + bB \rightleftharpoons cC + dD$

Then Equilibrium constant, $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Significance

The value of equilibrium constant K_c is important in predicting the extent of forward reaction or backward reaction of which a particular reaction proceeds. If K_c is too large then the reaction is more forward while small value of K_c implies that the reaction is more backward.

(b) Equation for the reaction: $Fe^{2+}_{(aq)} + Ag^{+}_{(aq)} \rightleftharpoons Ag_{(s)} + Fe^{3+}_{(aq)}$

As we are given with all reagents at the beginning of the reaction; we must firstly find reaction quotient (R_Q) so as to determine the direction to which the reaction proceed.

$$R_Q = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]} = \frac{0.3}{0.2 \times 0.1} = 15$$

But $K_c = 2.98$

So $Q_c > K_c$ and hence the reaction **proceed backward** to establish the equilibrium.

$Fe^{2+}_{(aq)} + Ag^{+}_{(aq)} \rightleftharpoons Ag_{(s)} + Fe^{3+}_{(aq)}$

	$Fe^{2+}_{(aq)}$	$Ag^{+}_{(aq)}$	$Fe^{3+}_{(aq)}$
Initially	0.1	0.2	0.3
At equilibrium	0.1 + x	0.2 + x	0.3 – x

$$K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]}$$

Then $\dfrac{0.3-x}{(0.2+x)\times(0.1+x)}=2.98$

Or $2.98x^2+1.894x-0.2404=0$ or $x=0.10843$

Hence at equilibrium:

$[Fe^{3+}]=0.19157M$

$[Ag^{+}]=0.30843M$

$[Fe^{2+}]=0.20843$

Question 9

(a) **Name of the law:** Equilibrium law
It states that: This is the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients.

(b)

	$3H_{2(g)}$	$+ N_{2(g)}$	$\rightleftharpoons 2NH_{3(g)}$
Initially	0	0	1
At equilibrium	3x	x	1 − 2x

n_T at equilibrium $3x+x+1-2x=(1+2x)$moles

Where 2x is numerically equal to the degree of dissociation.

$$K_p=\frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})}=\frac{(X_{NH_3}P_T)^2}{(X_{H_2}P_T)^3(X_{N_2}P_T)}=\frac{(X_{NH_3})^2}{(X_{H_2})^3(X_{N_2})P_T^2}$$

But $2x=0.95$ (95% NH_3 of dissociated into its elements); $x=0.475$

Then:

$$X_{NH_3}=\frac{1-2x}{1+2x}=0.026$$

$$X_{H_2}=\frac{3x}{1+2x}=0.731$$

$$X_{N_2}=\frac{x}{1+2x}=0.244$$

Then $2\times10^{-14}=\frac{0.026^2}{0.731^3\times0.244P_T^2}$ or $P_T=5.955\times10^5\,Pa$

Hence the pressure is $5.955\times10^5\,Pa$

(c) K_p will remain the same as the constant does not depend on the concentration of the reagents present in the system (like K_c, K_p is only temperature dependent).

Question 10

(a) Increase in temperature and decrease in temperature favour forward reaction for endothermic reaction and exothermic reaction respectively and vice versa.

(b)

	N_2	$+ O_2$	$\rightleftharpoons 2NO$
Initially	4	1	0
At equilibrium	4 – x	1 – x	2x

$$K_c=\frac{[NO]^2}{[\ N_2][O_2]}=\frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{4-x}{v}\right)\left(\frac{1-x}{v}\right)}=\frac{4x^2}{x^2-5x+4}=8\times10^{-4}$$

$3.9992x^2+0.004x-0.0032=0$ or $x=0.0278$

$$\%NO=\frac{n_{NO}}{n_T}\times100\%=\left(\frac{2x}{5}\right)\times100\%=1.112\%$$

Hence the percentage of nitrogen monoxide by volume is 1.112%

Question 11

(a) Equilibrium constant is the reaction quotient of the chemical system at equilibrium.
(b) Reaction equation;

$$CO_2(g) + C(g) \rightleftharpoons 2CO(g)$$

From which; $K_p = \frac{(P_{CO})^2}{P_{CO_2}}$

But by Dalton's law of partial pressure; $P_T = 4 = P_{CO} + P_{CO_2}$

From which; $P_{CO_2} = 4 - P_{CO}$

Then; $K_p = 10 = \frac{(P_{CO})^2}{4-P_{CO}}; (P_{CO})^2 + 10P_{CO} - 40 = 0$

Solving the above quadratic equation with P_{CO} as the unknown gives;

$P_{CO} = 3\text{atm}$ and therefore $P_{CO_2} = 4 - P_{CO} = (4-3)\text{atm} = 1\text{atm}$

Then; $X_{CO} = \frac{P_{CO}}{P_T} = \frac{3\text{atm}}{4\text{atm}} = 0.75$ and $X_{CO_2} = \frac{P_{CO_2}}{P_T} = \frac{1\text{atm}}{4\text{atm}} = 0.25$

The mole fraction of CO is 0.75

The mole fraction of CO_2 is 0.25

For gases; Volume ratio = Mole ratio (Avogadro's law)

It follows that; $\frac{V_{CO_2}}{V_T} \times 100 = \frac{n_{CO_2}}{n_T} \times 100 = 6$

But; $\frac{n_{CO_2}}{n_T} = X_{CO_2}$; so $X_{CO_2} = 0.06$ and $X_{CO} = 1 - X_{CO_2} = 1 - 0.06 = 0.94$

Then; $K_p = 10 = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(X_{CO}P_T)^2}{X_{CO_2}P_T} = \frac{(X_{CO})^2 P_T}{X_{CO_2}} = \frac{(0.94)^2 P_T}{0.06}$

From which the total pressure (P_T) is 0.68atm

Question 12

(a)
(i) Reaction for contact process

Reason

The reaction is accompanied with greater heat change.

(ii) Reaction for Haber process

Reason

Reaction is accompanied with greater change of number of gas molecules.

(b) $A + B \rightleftharpoons 2C$

At equilibrium $2 - x \quad 3 - x \quad 2x$

$$K_c = \frac{[C]^2}{[A][B]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{3-x}{v}\right)\left(\frac{2-x}{v}\right)} = \frac{4x^2}{x^2 - 5x + 6}$$

But $K_c = 4$

Then $4 = \frac{4x^2}{x^2-5x+6}$

Solving above equation gives $x = 1.2$ and $2x = 2 \times 1.2 = 2.4$moles

Hence number of moles of C at equilibrium is 2.4 moles

Question 13

(a) The reaction for contact process has smaller change of number of gas molecules implying that high pressure has less effect (compared to Haber process) while the higher heat change in the contact process ensures that the contact process respond more to temperature change.

(b) $N_2 + O_2 \rightleftharpoons 2NO$

At equilibrium $4 - x \quad 1 - x \quad 2x$

n_T at equilibrium $(4 - x) + (1 - x) + (2x) = 5\text{moles}$

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(X_{NO}P_T)^2}{(X_{N_2}P_T)(X_{O_2}P_T)} = \frac{(X_{NO})^2}{(X_{N_2})(X_{O_2})}$$

But $X_{NO} = \frac{2x}{5}$, $X_{N_2} = \frac{4-x}{5}$, $X_{O_2} = \frac{1-x}{5}$

Then $0.0008 = \frac{4x^2}{(4-x)(1-x)} = \frac{4x^2}{4-5x+x^2}$

Solving above equation gives $x = 0.028$

$$\% \text{ NO } = \left(\frac{2x}{5}\right) \times 100\% = \frac{2 \times 0.028}{5} \times 100\% = 1.12\%$$

Hence the percentage of nitric oxide is 1.12%

Question 14

(a)

1. It increases the percentage yield of ammonia.
2. It increases the rate of producing ammonia (ammonia is produced in shorter time).

(b) Equation for dissociation of N_2O_4 into NO_2: $N_2O_4 \rightleftharpoons 2NO_2(g)$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_2}} = \frac{(0.3\text{atm})^2}{(0.7\text{atm})} = 0.1286\text{atm}$$

If $P_T = 10\text{atm}$

By Dalton's law of partial pressure; $P_{NO_2} + P_{N_2O_4} = 10\text{atm}$

Then $0.1286 = \frac{(P_{NO_2})^2}{10-P_{NO_2}}$

$$(P_{NO_2})^2 + 0.1286P_{NO_2} - 1.286 = 0$$

This is the quadratic equation in P_{NO_2}; thus solving the equation gives $P_{NO_2} = 1.07\text{atm}$.

$$P_{N_2O_4} = 10 - P_{NO_2} = 8.93\text{atm}$$

Hence:

The partial pressure of NO_2 is 1.07atm

The partial pressure of N_2O_4 is 8.93atm

Alternative solution

$$K_p = \frac{(X_{NO_2}P_T)^2}{(X_{N_2O_4}P_T)} = \frac{(X_{NO_2})^2P_T}{(X_{N_2O_4})}$$

Where $P_T = 10\text{atm}$

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
At equilibrium	$1 - \alpha$		2α

$$X_{NO_2} = \frac{2\alpha}{1+\alpha} \quad \text{and} \quad X_{N_2O_4} = \frac{1-\alpha}{1+\alpha}$$

Then $K_p = \frac{4\alpha^2P_T}{1-\alpha^2} = \frac{4\times10\alpha^2}{1-\alpha^2} = 0.1286$

Solving above equation gives $\alpha = 0.0568$

$$P_{N_2O_2} = \left(\frac{1-\alpha}{1+\alpha}\right)P_T = \left(\frac{1-0.0568}{1+0.0568}\right)10\text{atm}$$

$$P_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right)P_T = \left(\frac{2\times0.0568}{1+0.0568}\right)10\text{atm} = 1.07\text{atm}$$

Hence

The partial pressure of NO_2 is 1.07atm

The partial pressure of N_2O_2 is 8.93atm

Question 15

(a) Temperature only.

(b) Increase in temperature increases the magnitude of equilibrium constant for endothermic reaction while it decreases the magnitude of equilibrium constant for exothermic reaction and vice-versa.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
At equilibrium	0.28atm		1.1atm

$$K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(1.1\text{atm})^2}{(0.28\text{atm})} = 4.32\text{atm}$$

Total pressure, P_1 at equilibrium $= P_{N_2O_4} + P_{NO_2}$ (By Dalton's law of partial pressure)

If the volume is doubled from V_1 to V_2 such that $V_2 = 2V_1$

By Boyle's law; $P_1V_1 = P_2V_2$

$P_2 = \frac{P_1V_1}{V_2} = \frac{P_1V_1}{2V_1} = \frac{P_1}{2}$

For N_2O_4; $P_2 = \frac{0.28\text{atm}}{2} = 0.14\text{atm}$

For NO_2; $P_2 = \frac{1.1\text{atm}}{2} = 0.55\text{atm}$

The decrease in pressure will shift equilibrium position to the NO_2 side.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
At new equilibrium	$0.14 - x$		$0.55 + 2x$

Then; $4.32 = \frac{(0.55+2x)^2}{0.14-x}$

From which; $4x^2 + 6.52x - 0.3023 = 0;\ x = 0.045$

Hence at new equilibrium:

Partial pressure of $N_2O_4 = 0.14 - 0.045 = (0.14 - 0.045)\text{atm} = 0.095\text{atm}$

Partial pressure of $NO_2 = 0.55 + 2x = (0.55 + 2 \times 0.045)\text{atm} = 0.64\text{atm}$

Question 16

(a)

(i) No effect.
(ii) The percentage yield will increase.
(iii) No effect.

(b)	$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g)$	$+ O_2(g)$
At equilibrium	$1 - 2x$		$2x$	x

Where $\alpha = \frac{2x}{1} = 0.5,\ x = 0.25$

$P_{O_2} = X_{O_2}P_T = \left(\frac{x}{1+x}\right) 1\text{atm} = 0.2\text{atm}$

$P_{SO_2} = X_{SO_2}P_T = \left(\frac{2x}{1+x}\right) 1\text{atm} = 0.4\text{atm}$

$P_{SO_3} = X_{SO_3}P_T = \left(\frac{1-2x}{1+x}\right) 1\text{atm} = 0.4\text{atm}$

$K_P = \frac{(P_{SO_2})^2(P_{O_2})}{(P_{SO_3})^2} = \frac{0.2 \times 0.4^2}{0.4^2} = 0.2\text{atm}$

Hence K_p is 0.2atm

$K_c = K_p(RT)^{m-n}$ for $m = 2$ and $n = 3$

$K_c = K_p(RT)^{2-3} = K_P(RT)^{-1}$ or $K_C = \frac{K_P}{RT} = \frac{0.2}{0.082 \times 523} = 4.66 \times 10^{-3}\text{moldm}^{-3}$

Hence K_c is $4.66 \times 10^{-3}\text{moldm}^{-3}$

Question 17

(a)

(i) It increases the rate of both forward and backward reaction by the same amount.
(ii) A: To increase the production rate of ammonia.
B: To reduce the production cost of ammonia.

$SO_2Cl_2(g)$	$\rightleftharpoons$	$SO_2(g)$	$+ Cl_2(g)$
$1 - \alpha$		α	α

Where α is numerically equal to the degree of dissociation = 0.9

$P_{SO_2} = X_{SO_2}P_T = \left(\frac{\alpha}{1+\alpha}\right) P_T = \left(\frac{0.9}{1+0.9}\right) 1\text{atm} = 0.474\text{atm} = P_{Cl_2}$

$P_{SO_2Cl_2} = \left(\frac{1-\alpha}{1+\alpha}\right) P_T = \left(\frac{1-0.9}{1+0.9}\right) \times 1\text{atm} = 0.053\text{atm}$

$K_p = \frac{(P_{SO_2})(P_{Cl_2})}{(P_{SO_2Cl_2})} = \frac{0.474 \times 0.474}{0.053} = 4.239\text{ atm}$

Hence numerical value of K_p is 4.239

Question 18

(a) Catalyst affect chemical equilibrium by enabling the equilibrium to be reached earlier. It has no effect on the **position** of chemical equilibrium (not chemical equilibrium in general).

(b)

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

At equilibrium $\quad 1-2x \quad 2x \quad x$

But $\alpha = \frac{2x}{1} = 0.4$ or $x = 0.2$

Atmospheric pressure $= 1$ atm

$P_{CO} = X_{CO}P_T = \left(\frac{2x}{1+x}\right) \times 1\text{atm} = 0.33\text{atm}$

$P_{O_2} = X_{O_2}P_T = \left(\frac{x}{1+x}\right) \times 1\text{atm} = 0.17\text{atm}$

$P_{CO_2} = X_{CO_2}P_T = \left(\frac{1-2x}{1+x}\right) \times 1\text{atm} = 0.5\text{atm}$

$K_p = \frac{(P_{CO})^2(P_{O_2})}{(P_{CO_2})^2} = \frac{(0.33)^2(0.17)}{(0.5)^2} = 7.4 \times 10^{-2}\text{atm}$

Hence the dissociation constant (K_p) for the reaction is 7.4×10^{-2}atm

Question 19

(a) $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$

At the equilibrium; rate of forward reaction=rate of backward reaction

That is $K_f[NO]^2\,[O_2] = K_b\,[NO_2]^2$

From which $\frac{K_f}{K_b} = \frac{[NO_2]^2}{[NO_2]^2[O_2]} = K_c$

Substituting $\frac{2.6\times10^3 L^2 mol^{-2} s^{-1}}{4.1\,L\ mol^{-1}\,s^{-1}} = K_c$

(b) Hence the value of equilibrium constant is $634.15L\ \ mol^{-1}$

(c) $\frac{1}{2}\frac{d[NO_2]}{dt} = R = K[NO]^2[O_2]$

$= 2.6 \times 10^3 \times (0.006)^2 \times 0.29$ or $0.027Ms^{-1}$

Then $\frac{d[NO_2]}{dt} = 2R = 2 \times 0.027Ms^{-1}$

Hence the rate of the production of NO_2 is $0.054Ms^{-1}$

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

$0 \quad 0 \quad 0.2$

$2x \quad x \quad 0.2 - 2x$

But $\frac{2X}{0.2} = 0.15$ or $x = 0.015$mol

Then $[NO_2] = \frac{(0.2-2\times0.015)}{5L}$mol $= 0.034M$

$[O_2] = \frac{0.015mol}{5L} = 0.003M$

$[NO] = \frac{2\times0.015mol}{5L} = 0.006M$

Then using $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{(0.034M)^2}{(0.006M)^2\times0.003M} = 1.07 \times 10^4M^{-1}$

Hence the value of the equilibrium constant is $1.07 \times 10^4M^{-1}$

Question 20

(a) (i) It explains effect of different factors on the position of chemical equilibrium.
(ii) It describes the relationship between concentration of reactants and that of products when the chemical system of reversible reaction is allowed to attain the equilibrium. .

(b) (i) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$ (ii) $K_p = \frac{(NO_2)^2}{(N_2O_4)}$

(iii) $K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(P_{NO_2})^2}{2.71atm} = 0.133atm$

$(P_{NO_2})^2 = 0.36043atm^2$; $P_{NO_2} = \sqrt{0.36043atm^2} = 0.6atm$

Equilibrium pressure of NO_2 is 0.6atm

Question 21

(a)

(i) Represents the ratio of product of concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients obtained in the course of the chemical reaction.
(ii) Represents the temperature dependent fixed ratio which is obtained as the quotient of the product of equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficient.

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

	PCl_5	PCl_3	Cl_2
Pressure at $t = 0$	P_0	0	0
Pressure at equilibrium	$P_0 - P$	P	P

(Since pressure is directly proportional to the number of moles, pressure ratio is equal to the mole ratio and therefore pressure can be treated as moles in the equation).

Also from, pressure-mole relationship:

Degree of dissociation, $\alpha = \frac{P}{P_0}$

And $\alpha = 20\% = 0.2$ (PCl_5 dissociated to 80%)

Thus $0.2 = \frac{P}{P_0}$ or $P = 0.2P_o$

Total pressure at equilibrium; $P_o - P + P + P = 1.5$ or $P_o + P = P_o + 0.2P_0 = 1.2P_0 = 1.5$

From which $P_o = 1.25$ atm

And $P = 0.2P_o = 0.2 \times 1.25 \text{ atm} = 0.25$ atm

Hence:

Partial pressure of $PCl_5 = P_o - P = (1.25 - 0.25)\text{atm} = 1$ atm

Partial pressure of $PCl_3 = P = 0.25$ atm

Partial pressure of $Cl_2 = P = 0.25$ atm

Question 22

(a) By adding hydrogen gas.

Explanation:

Decreasing volume of the container has no effect on the position of chemical equilibrium. This is because the decrease in volume will increase the total pressure of the system and since the reaction is not accompanied with change in number of gas molecules, the change in pressure has no effect on the position of equilibrium and thus no effect on the yield of HI too. However according to Le-Chatelier's principle, the increase in concentration of hydrogen gas shift the position of equilibrium to HI side and therefore increasing the yield of HI.

(b) For gases, the most common method of representing equilibrium constant is K_P. So the given value of Equilibrium constant is K_P value.

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$

	N_2	O_2	NO_2
At $t = 0$	2	2	0
At equilibrium	$2 - x$	$2 - 2x$	$2x$

$K_p = 4.3 \times 10^{-3}$

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2})(P_{O_2})^2} = \frac{(X_{NO_2}P_T)^2}{(X_{N_2}P_T)(X_{O_2}P_T)^2} = \frac{(X_{NO_2})^2}{(X_{N_2})(X_{O_2})^2 P_T}$$

Using $X = \frac{n}{n_T}$

Where $n_T = 2 - x + 2 - 2x + 2x = 4 - x$

Then; $K_p = \frac{\left(\frac{2x}{4-x}\right)^2}{\left(\frac{2-x}{4-x}\right)\left(\frac{2-2x}{4-x}\right)^2 \times 1} = 4.3 \times 10^{-3}$

$$\frac{4x^2(4-x)}{(2-x)(2-2x)^2} = 4.3 \times 10^{-3}$$

$$\frac{16x^2 - 4x^3}{8 - 20x + 16x^2 - 4x^3} = 4.3 \times 10^{-3}$$

From which; $3.982x^3 - 15.9312x^2 - 0.086x + 0.0344 = 0$

Solving the above equation, gives the practical value of x which is 0.044.

Hence the composition of each is as follows:

Number of moles of $N_2 = 2 - x = 1.956$ mol.

Number of moles of $O_2 = 2 - 2x = 1.912$ mol.

Number of moles of $NO_2 = 2x = 0.088$ mol.

Question 23

(a)

(i) White fumes (of hydrogen chloride gas).

(ii) HCl being gaseous is removed from the equilibrium system and thus the position of equilibrium shifts to the right.

(b) Given that:

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)\ K_c = 10^2$....... (i)

From which: $K_c = \frac{[NO]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}} = K_1 = 10^2$

$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g) K_C = 10^3$........ (ii)

From which: $K_c = \frac{[N_2O_4]}{[NO]^2[O_2]} = K_2 = 10^3$

$N_2O_4(g) \rightleftharpoons 2NO_2(g) K_C = 10^4$ .... (iii)

From which: $K_c = \frac{[NO_2]^2}{[N_2O_4]} = K_3 = 10^4$

Taking 2(i) + (ii) + (iii) gives

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ which is the same as given equation whose K_c is unknown.

Thus the K_c of the given equation will be given by the following relationship:

Required $K_c = (k_1)^2 k_2 k_3 = (10^2)^2 \times 10^3 \times 10^4 = 10^{11}$

Hence the equilibrium constant is 10^{11}

Question 24

(a) "When a chemical system is allowed to reach the equilibrium at a particular temperature, there is a fixed ratio of product of concentration of products to that of reactants raised to powers equals to stoichiometric coefficients regardless to the original concentration of the reagents present in the system."

For the hypothetical reaction: $aA + bB \rightleftharpoons cC + dD$

Then according to equilibrium law; $\frac{[C]^c[D]^d}{[A]^a[B]^b} = \text{Constant } (K_c)$

(b)

(i) $K_c = \frac{[R]^2}{[P][Q]^2}$

(ii) $[P] = \frac{3.82mol}{10dm^3} = 0.382moldm^{-3}$; $[R] = \frac{5.24mol}{10dm^3} = 0.524moldm^{-3}$

$K_c = 68.0mol^{-1}dm^3 = \frac{(0.524moldm^{-3})^2}{0.382moldm^{-3} \times [Q]^2}$

From which; $[Q] = 0.103moldm^{-3}$

(iii) The equilibrium amount of P will increase while the K_c value will decrease.

(iv) The equilibrium amount of P will increase.

(v) $K_c = \frac{[P][Q]^2}{[R]^2} = \frac{1}{\frac{[R]^2}{[P][Q]^2}} = \frac{1}{68.0mol^{-1}dm^3} = 0.0147moldm^{-3}$

Question 25

(a)

(i)

First feature: Rate of forward reaction is equal to the rate of backward reaction.

Second feature: Concentration of reagents present in the system remain unchanged.

(ii) Heating will force the system to resist the change by absorbing the heat and therefore favouring forward reaction which is endothermic and hence more NO_2 which appears in brown colouration will be formed.

(iii) Increasing the pressure will force the system to resist the change by shifting the equilibrium position to the side with fewer gas molecules (N_2O_4 side) and hence the amount of NO_2 decreases.

(b) Using $n = \frac{m}{M_r}$;

Initial number of moles of $CH_3COOH = \frac{24.4g}{60gmol^{-1}} = 0.4mol$

Initial number of moles of $CH_3CH_2OH = \frac{24.3g}{46gmol^{-1}} = 0.53mol$

CH_3COOH reacts with NaOH according to the following equation; $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

From which mole ratio of NaOH to CH_3COOH is 1:1

Thus $n_{NaOH} = n_{CH_3COOH} = \frac{26.5}{1000} \times 0.4mol = 0.0106mol$

Whence number of moles of CH_3COOH in $25cm^3$ of the solution is 0.0106mol.

Then number of moles of CH_3COOH in $250cm^3$ of the solution $= \frac{0.0106 \times 250}{25}mol = 0.106mol$

Hence number of moles of CH_3COOH at equilibrium was 0.106mol

	$CH_3COOH(l)$ +	$CH_3CH_2OH(l)$ ⇌	$CH_3COOCH_2CH_3(l)$ +	$H_2O(l)$
Initially	0.4	0.53	0	0
At equilibrium	0.4 – x	0.53 − x	x	x

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.4-x}{V}\right)\left(\frac{0.53-x}{V}\right)} = \frac{x^2}{(0.4-x)(0.53-x)}$$

But $0.4 - x = 0.106$; $x = 0.294$

Substituting; $K_c = \frac{0.294^2}{(0.4-0.294)(0.53-0.294)} = 3.46$

Hence the equilibrium constant is 3.46

Question 26

(a) **In terms of Le-Chatelier's principle:** To decrease the applied high pressure the equilibrium position will shift to the side with fewer gas particles (ammonia side) by producing more ammonia and hence high pressure has an advantage of increasing the ammonia yield in the Haber process.

In terms of behaviour of particles: High pressure makes gases to be more compressed into smaller volume and therefore more concentrated leading to greater collision frequency and hence higher reaction rate. So high pressure has another advantage of increasing the rate of ammonia production in the Haber process.

(b)

(i) $K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]}$

(ii) At equilibrium:

$n_{Acid} = 1 - x$; $n_{Ethanol} = 2 - x$

$n_{Ester} = x$; $n_{Water} = 5 + x$

But $n_{Ester} = x = 0.54mol$;

Thus $n_{Water} = 5 + x = (5 + 0.54) = 5.54mol$

The number of moles of water is 5.54mol

(iii) $K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{5+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{2-x}{V}\right)} = \frac{x^2+5x}{x^2-3x+2}$

Substituting; $K_c = \frac{0.54^2+5(0.54)}{0.54^2-3(0.54)+2} = 4.45$

The value for K_c is 4.45

The K_c value has no units because there is an equal number of molecules in either side (reactants side and products side) of the reaction equation.

(iv) A: The amount will decrease.
B: The time will decrease.
C: The value will decrease.

Question 27

(a)

(i) *Is the condition which occurs in the reversible reaction when the rate of forward reaction is equal to the rate of reverse reaction.* In this case the equilibrium occurs when the rate of consumption of 3-menthlybutanoic acid and ethanol is equal to the rate of producing ester and water at which concentration of all reagents (acid, ethanol, ester and water) remain unchanged.

(ii) In order to increase the yield of ester. This is because, according to Le-Chatelier's principle; using high concentration of ethanol shifts equilibrium position to ester side (side with lower concentration) and therefore forming more ester.

(iii) Catalyst enable the equilibrium to be reached in shorter time. However, it has no effect in equilibrium position because it increases the rate of both forward and reverse reaction by equal amount.

(b)

	$CO(g)$ +	$H_2O(g)$ ⇌	$CO_2(g)$ +	$H_2(g)$
Number of moles (At = 0)	3	1	0	0
Number of moles (at equilibrium)	3 – x	1 – x	x	x

$$K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = \frac{(X_{CO_2}P_T)(X_{H_2}P_T)}{(X_{CO}P_T)(X_{H_2O}P_T)}$$

$$K_p = \frac{(X_{CO_2})(X_{H_2})}{(X_{CO})(X_{H_2O})} = \frac{\left(\frac{n_{CO_2}}{n_T}\right)\left(\frac{n_{H_2}}{n_T}\right)}{\left(\frac{n_{CO}}{n_T}\right)\left(\frac{n_{H_2O}}{n_T}\right)} = \frac{n_{CO_2} \times n_{H_2}}{n_{CO} \times n_{H_2O}}$$

$$K_p = 0.65 = \frac{(x)(x)}{(3-x)(1-x)} = \frac{x^2}{x^2 - 4x + 3}$$

From which $0.37x^2 + 2.52x - 1.89x = 0$

Solving above equation gives practical value of x which is 0.68

(i) Hence the number of moles of H_2 is 0.68mol

(ii) $n_T = (3 - x) + (1 - x) + x + x = 4\text{mol}$

$$P_{CO} = X_{CO}P_T = \left(\frac{n_{CO}}{n_T}\right)P_T = \left(\frac{3-x}{4}\right)P_T$$

Substituting; $P_{CO} = \left(\frac{3-0.68}{4}\right)2\text{atm} = 1.16\text{atm}$

Similarly; $P_{H_2O} = \left(\frac{n_{H_2O}}{n_T}\right)P_T = \left(\frac{1-X}{4}\right)P_T = \frac{(1-0.68)}{4} \times 2\text{atm} = 0.16\text{atm}$

$$P_{H_2} = P_{CO_2} = \left(\frac{x}{4}\right)P_T = \left(\frac{0.68}{4}\right) \times 2\text{atm} = 0.34\text{atm}$$

Hence:

Partial pressure of CO = 1.16atm

Partial pressure of H_2O = 0.16atm

Partial pressure of H_2 = 0.34atm

Partial pressure of CO_2 = 0.34atm

Question 28

(a) Lower temperature.

Reason

K_p is larger at the lower temperature.

(b)

(i) $K_c = \frac{[H_2][I_2]}{[HI]}$

(ii) V cancels in the K_c expression (as the reaction is not accompanied by change in number of moles of reagents present in the system).

(iii)

	$2HI_{(g)} \rightleftharpoons$	$H_{2(g)} +$	$I_{2(g)}$
Initially	0.218	0	0
At equilibrium	$0.218 - 2x$	x	x

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.218-2x}{V}\right)^2} = \frac{x^2}{(0.218-2x)^2}$$

But $x = 0.023$ (Amount of hydrogen at equilibrium)

$$K_c = \frac{(0.023)^2}{\left(0.218 - 2(0.023)\right)^2} = 0.0179$$

The value of K_c is 0.0179

(iv) $K_c = \frac{[HI]^2}{[H_2][F_2]} = \frac{1}{\frac{[H_2][F_2]}{[HI]^2}} = \frac{1}{0.0179} = 55.9$

The value of K_c is 55.9

Question 29

(a) $I < II < III$ $\longrightarrow$

Increase in tendency of forming products

(b) $K_c = \frac{K_f}{K_r} = \frac{0.13^{-1}s^{-1}}{6.02 \times 10^{-4}s^{-1}} = 215.9M^{-1}$

The value of equilibrium constant is $215.9M^{-1}$

(c) From the given reaction equation;

(i) $K_p = P_{CO_2} = 0.236\text{atm}$

(ii) $\Delta n = 1 - 0 = 1$

Then $K_P = K_c(RT)^{\Delta n} = K_c(RT)^1$

Substituting;$0.236\text{atm} = K_c \times 0.082\text{atmLmol}^{-1K^{-1}} \times 1073K$

From which K_c=$2.68 \times 10^{-3}\text{moldm}^{-3}$

Question 30

(a)

(i) Remain the same
(ii) Decrease
(iii) Increase
(iv) Remain the same
(v) Increase

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

	$PCl_5(g)$	$PCl_3(g)$	$Cl_2(g)$
Pressure at t = o	1.66	0	0
Pressure at equilibrium	$166 - x$	x	x

$$K_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})}$$

Substituting; $0.497 = \frac{(x)(x)}{1.66-x} = \frac{x^2}{1.66-x}$

From which; $x^2 + 0.497x - 0.82502 = 0;\ x = 0.693$

Hence:

Partial pressure of $P_{PCl_3} = x = 0.693atm$

Partial pressure of $Cl_2 = x = 0.693atm$

Partial pressure of $P_{PCl_5} = 1.66 - x = 0.967atm$

Question 31

(a) From ideal gas equation; $P = \frac{nRT}{V}$

Then; $P_{initial} = \frac{n_{H_2O}RT}{V} = \frac{0.1 \times 0.082 \times 1153atm}{1} = 9.4546atm$

$C(s) \quad + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

	$H_2O(g)$	$CO(g)$	$H_2(g)$
Initial pressure	9.4546	0	0
Equilibrium pressure	$9.4546 - x$	x	x

$$K_p = 14.1 = \frac{(P_{CO})(P_{H_2})}{(P_{H_2O})} = \frac{x^2}{9.4546 - x}$$

From which; $x^2 + 14.1x - 133.3 = 0; x = 6.5$

Hence:

Partial pressure of $CO = x = 6.5atm$

Partial pressure of $H_2 = x = 6.5atm$

Partial pressure of $H_2O = 9.4546 - x = 2.95atm$

(b) Amount of $H_2O(g)$ reacted is equivalent to the pressure of 6.5atm (decrease in pressure)

Using; $n = \frac{PV}{RT}$

$$n_{H_2O} \text{ reacted } = \frac{6.5 \times 1mol}{0.082 \times 1153} = 0.069mol$$

From the reaction equation, mole ratio of $C(s)$ to $H_2O(g)$ is 1:1

So number of moles of $C(s)$ required to react with 0.069mol was also 0.069mol.

Using $m = nM_r$;

Minimum amount of $C(s)$ required is $0.069mol \times 12gmol^{-1} = 0.83g$

Question 32

(a) Exothermic

Explanation:

K_r increases more than K_f when temperature is increased. This means that E_a of reverse reaction is greater than E_a of forward reaction. The reaction is exothermic when E_a(reverse) $>$ E_a(forward).

(b) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

At equilibrium 0.8 0.1 0.6 0.4

$$K_c = \frac{[SO_2][NO]}{[SO_2][NO_2]} = \frac{\left(\frac{0.6}{V}\right)\left(\frac{0.4}{V}\right)}{\left(\frac{0.8}{V}\right)\left(\frac{0.1}{V}\right)} = 3$$

Addition of 1 mole of NO to the equilibrium mixture will favour reverse reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

After addition of 1mol of NO 0.8 0.1 0.6 1.4

At new equilibrium $0.8 + x$ $0.1 + x$ $0.6 - x$ $1.4 - x$

Then;

$$K_c = 3 = \frac{\left(\frac{0.6 - x}{V}\right)\left(\frac{1.4 - x}{V}\right)}{\left(\frac{0.8 + x}{V}\right)\left(\frac{0.1 + x}{V}\right)}$$

From which; $2x^2 + 4.7x - 0.6 = 0$; $x = 0.12$

Hence at new equilibrium (by substituting $x = 0.12$):

Number of moles of $SO_2 = 0.8 + x = 0.92\text{mol}$

Number of moles of $NO_2 = 0.1 + x = 0.22\text{mol}$

Number of moles of $SO_3 = 0.6 - x = 0.48\text{mol}$

Number of moles of $NO = 1.4 - 4 = 1.28\text{mol}$

Question 33

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Initially 1 0 0

At equilibrium $1 - \alpha$ α α

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{\left(\frac{1-\alpha}{V}\right)} = \frac{\alpha^2}{(1-\alpha)V}$$

But $\alpha = \frac{78.5}{100} = 0.785$ and $V = 5L$

$$K_c = \frac{0.785^2}{(1 - 0.785) \times 5}\text{mol/L} = 0.573\text{mol/L}$$

$K_p = K_c(RT)^{\Delta n}$ where $\Delta n = 2 - 1 = 1$

$K_p = 0.573\text{molL}^{-1} \times 0.082\text{atmLmol}^{-1}\text{K}^{-1} \times 500\text{K} = 23.5\text{atm}$

The value of K_p is 23.5atm

(b) $Q_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.15M \times 0.6M}{0.5M} = 0.18M$

So $Q_c(0.18) < K_c(0.573M)$ and hence **the reaction will proceed in forward direction to reach the equilibrium.**

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At new equilibrium $0.5 - x$ $0.15 + x$ $0.6 + x$

$$K_c = 0.573 = \frac{(0.15 + x)(0.6 + x)}{(0.5 - x)}$$

From which: $x^2 + 1.323x - 0.1965 = 0$; $x = 0.135$

Hence at the new equilibrium (by substituting x=0.135):

$[PCl_5] = 0.5 - x = 0.365M$

$[PCl_3] = 0.15 + x = 0.285M$

$[Cl_2] = 0.6 + x = 0.735M$

Question 34

(a)

(i) Increasing concentration of N_2(adding N_2)
(ii) Increasing concentration of H_2(adding H_2)
(iii) Increasing temperature
(iv) Increasing pressure

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

	PCl_5	PCl_3	Cl_2
Initially	1	0	0
At equilibrium	$1-\alpha$	α	α

$$K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{(X_{PCl_3}P_T)(X_{Cl_2}P_T)}{(X_{PCl_5}P_T)}$$

$$K_p = \frac{\left(\frac{n_{PCl_3}}{n_T}\right)\left(\frac{n_{Cl_2}}{n_T}\right)P_T}{\left(\frac{n_{PCl_5}}{n_T}\right)} = \frac{(n_{PCl_3})(n_{Cl_2})P_T}{(n_{PCl_5})(n_T)}$$

$$K_p = 1.78 = \frac{\alpha\times\alpha}{(1-\alpha)(1+\alpha)}(n_T = 1-\alpha+\alpha+\alpha = 1+\alpha)$$

$$= \frac{\alpha^2}{1-\alpha^2}$$

From which; $2.78\alpha^2 = 1.78; \alpha = 0.8$

Thus the degree of dissociation (α) is 0.8

Then using $\alpha = \frac{i-1}{N-1}$

Where: is the Van't Hoff's factor,

N is the number of molecules formed after dissociation of 1 molecule of $PCl_5 = 2$

Substituting $0.8 = \frac{i-1}{2-1}; i = 1.8$

But also; $i = \frac{\text{Expected } M_r}{\text{Observed } M_r}$

Where; expected M_r = Molar mass of PCl_5 before dissociation $= \big(31 + (5\times 35.5)\big)gmol^{-1} = 208.5gmol^{-1}$

Then $1.8 = \frac{208.5gmol^{-1}}{\text{Observed } M_r}$; Observed $M_r = 115.8gmol^{-1}$

From ideal gas equation; $\rho = \frac{PM_r}{RT}$

Thus density of the mixture (density of PCl_5 after dissociation) $= \frac{1atm\times 115.8gmol^{-1}}{0.082atmLmol^{-1}K^{-1}\times 523K} = 2.7gL^{-1}$

Density of the equilibrium mixture is 2.7g/L

Question 35

(a) $K_p = \frac{(P_{CO_2})^4}{(P_{C_2H_6})^2(P_{O_2})^7}$

But from ideal gas equation; P = [ ]RT

$$\text{Then } K_p = \frac{([CO_2]RT)^4}{([C_2H_6]RT)^2([O_2]RT)^7}$$

$$K_p = \frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7}\times(RT)^{4-(2+7)}$$

$$\text{But } \frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7} = K_c$$

Hence $K_p = K_c(RT)^{-5}$

(b) Initial total pressure $= P_{H_2} = \frac{n_{H_2}RT}{V} = \frac{0.2\times 0.082\times 363}{1}atm = 5.9532atm$

$H_2(g) + S(s) \rightleftharpoons H_2S(g)$

	H_2	H_2S
Initial pressure	5.9532	0
Equilibrium pressure	$5.9532-x$	x

$$K_p = \frac{P_{H_2S}}{P_{H_2}} = \frac{x}{5.9532-x} = 6.8\times 10^{-2}$$

From which ; $1.068x = 0.4048; x = 0.379$

The partial pressure of H_2S is 0.379atm

Question 36

(a) This is because the increase in temperature does not increase values of K_f and K_b by the same amount due to the difference in activation energy of forward and backward reaction. If the activation energy of forward reaction is greater than that of backward reaction (for endothermic reactions), the increase in K_f value will be greater than that of K_b and therefore the K_c value will increase while the K_c value will decrease if the activation energy of forward reaction is smaller (for exothermic reactions).

(b) From ideal gas equation: $M_r = \frac{mRT}{VP} = \frac{\rho RT}{P}$

Then $M_{mixture} = \frac{3.2 \times 0.0821 \times 800}{3.6} g/mol = 58.3822 g/mol$

$i = \frac{\text{Expected } M_r}{\text{Observed } M_r} = \frac{80 g/mol}{58.3822 g/mol} = 1.37$

But also $i = \frac{P_{observed}}{P_{expected}} = \frac{3.6}{P_{expected}} = 1.37$

From which $P_{expected} = \frac{3.6}{1.37} atm = 2.63 atm$

From $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$;

$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2$; $N = 1.5$

$\alpha = \frac{i-1}{N-1} = \frac{1.37-1}{1.5-1} = 0.74$

	$2SO_3(g)$	$\rightleftharpoons 2SO_2(g)$	$+ O_2(g)$
Initial pressure	2.63	0	0
Equilibrium pressure	$2.63 - 2x$	$2x$	x

But $\alpha = \frac{2x}{2.63} = 0.74$; $x = 0.9731$

Equilibrium pressure for each:

$P_{SO_2} = 2.63 - 2x = 0.6838 atm$

$P_{SO_2} = 2x = 1.9462 atm$,

$P_{O_2} = x = 0.9731 atm$

$$K_p = \frac{(P_{SO_2})^2 \times P_{O_2}}{(P_{SO_3})^2} = \frac{(1.9462 atm)^2 \times 0.9731 atm}{(0.6838 atm)^2} = 7.88 atm$$

The K_p value is 7.88atm.

Question 37

(a) Yes; it is correct. When the system is at equilibrium, the reaction quotient becomes equal to an equilibrium constant which is constant at given temperature.

(b)

	I_2	$+ H_2$	$\rightleftharpoons 2HI$
At equilibrium	$2.98 - x$	$8.1 - x$	$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{4x^2}{(2.98 - x)(8.1 - x)}$$

But $2x = 5.64$ (Amount of HI at equilibrium); $x = 2.82$

Substituting the value of *x* to above K_c expression gives $K_c = 37.65$

If we start with 5.3 moles of I_2 and 7.94 moles of H_2

	I_2	$+ H_2$	$\rightleftharpoons 2HI$
At equilibrium	$5.3 - x$	$7.94 - x$	$2x$

Then; $37.65 = \frac{4x^2}{(5.3 - x)(7.94 - x)}$

Solving above equating gives; $x = 4.62 mol$ and $2x = 2 \times 4.62 mol = 9.24 mol$

Hence number of moles of HI formed is 9.24moles

Question 38

(a)

(i) $4C + 3D \rightleftharpoons 3A + 2B$

(ii) Units of $K_c = \frac{(\text{Units of }[A])^3(\text{Units of }[B])^2}{(\text{Units of }([C])^4(\text{Units of }[D])^3}$

Units of $K_c = \frac{(\text{moldm}^{-3})^3(\text{moldm}^{-3})^2}{(\text{moldm}^{-3})^4(\text{moldm}^{-3})^3} = (\text{moldm}^{-3})^{-3} = \mathbf{dm^9mol^{-3}}$

(iii) The reaction is exothermic.

(b) Reaction equation:

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

Initial pressure	P	0	0
Pressure at equilibrium	P − 2x	2x	x

Where $P_T = P - 2x + 2x + x = P + x = 0.28\text{atm}$

But $\frac{2x}{P} \times 100 = 33.33;\ x = 0.16665P$

Then $P + x = P + 0.16665P = 0.28\text{atm};\ P = 0.24\text{atm}$

Thus at equilibrium:

$P_{NOBr} = P - 2x = 0.24\text{atm} - (2 \times 0.16665 \times 0.24)\text{atm} = 0.16\text{atm}$

$P_{NO} = 2x = 2 \times 0.16665 \times 0.24\text{atm} = 0.08\text{atm}$

$P_{Br_2} = x = 0.16665 \times 0.24\text{atm} = 0.04\text{atm}$

$K_p = \frac{(P_{NO})^2 \times P_{Br_2}}{(P_{NOBr})^2} = \frac{(0.08\text{atm})^2 \times 0.04\text{atm}}{(0.16\text{atm})^2} = 0.01\text{atm}$

The K_p is 0.01atm

Question 39

(a) $4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$

(b)

(i) $K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$

(ii) From $M_r = \frac{mRT}{PV}$

Where: $m = 2.585g, V = 1dm^3 = 10^{-3}\ m^3, R = 8.314,$

$P = 1.01 \times 10^5\ N/m^2;\ T = 60°C = (60 + 273)\ K = 333K$

Then observed molar of the gas $= \frac{2.585 \times 8.314 \times 333}{1.01 \times 10^5 \times 10^{-3}} g/mol = 70.86 g/mol$

$i = \frac{\text{Expected molar mass of the gas}}{\text{observed molar mass of the gas}}$

But expected molar mass of N_2O_4 is 92g /mol

Thus $i = \frac{92}{70.86} = 1.3$

Using $\alpha = \frac{i-1}{N-1}$ where $N = 2$

$\alpha = \frac{1.3 - 1}{2 - 1} = 0.3$ or 30%

Hence degree of dissociation of N_2O_4 is 30%

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

At equilibrium $1 - \alpha$ 2α

$n_T = (1 - \alpha) + 2\alpha = (1 + \alpha)\text{moles}$

$P_{N_2O_4} = \left(\frac{1 - \alpha}{1 + \alpha}\right) P_T = \left(\frac{1 - 0.3}{1 + 0.3}\right) \times 1.01 \times 10^5 = 5.44 \times 10^4 Nm^{-2}$

$P_{NO_2} = \left(\frac{2\alpha}{1 + \alpha}\right) P_T = \left(\frac{2 \times 0.3}{1 + 0.3}\right) \times 1.01 \times 10^5 = 4.66 \times 10^4 Nm^{-2}$

Using K_p expression in (i) above:

$K_p = \frac{(4.66 \times 10^4)^2}{5.44 \times 10^4} Nm^{-2} = 3.99 \times 10^4 Nm^{-2}$

Question 40

(a) The amount of $CaCO_3$ must be so small that even after its complete decomposition it produces small amount of CO_2 with partial pressure which is less than K_p.

(b)

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

	O_2	SO_2	SO_3
Initially	0 .1	0.2	0
At equilibrium	$0.1 - x$	$0.2 - 2x$	$2x$

At equilibrium $n_T = (0.1 - x) + (0.2 - 2x) + 2x = (0.3 - x)$ moles

But $\frac{(n_{O_2} + n_{SO_2})}{n_T} \times 100 = 10$

$\frac{(0.1-x)+(0.2-2x)}{0.3-x} = 0.1$ or $0.3 - 3x = 0.03 - 0.1x$ or $x = 0.093$ moles

Hence at equilibrium:

Amount of $O_2 = 0.1 - x = 0.0069$ moles

Amount of $SO_2 = 0.2 - 2x = 0.0138$ moles

Amount of $SO_3 = 2x = 0.1862$ moles

By Dalton's law of partial pressure: $P_T = P_{O_2} + P_{SO_2} + P_{SO_3}$

$$P_T = \frac{n_{O_2}RT}{V} + \frac{n_{SO_2}RT}{V} + \frac{n_{SO_3}RT}{V}$$

$$P_T = (n_{O_2} + n_{SO_2} + n_{SO_3})\frac{RT}{V}$$

$$P_T = \frac{n_T RT}{V}$$

But of equilibrium $n_T = (0.3 - x) = 0.2069$moles

Then; $P_T = \frac{0.2069 \times 0.082 \times 311}{0.2}$atm $= 26.38$atm

Hence the pressure of the system at equilibrium is 26.38 atm.

Question 41

(a) 100% yield implies that the magnitude of equilibrium constant is **infinitely large.**

(b) Initially:

Number of moles of $[SOCl_2] = \frac{23.8}{119} = 0.2$ moles

Number of moles of $[SO] = \frac{19.2}{48} = 0.4$ moles

Number of moles of $[Cl_2] = \frac{142}{71} = 2$ moles

Thus at the beginning of the reaction:

Using $[\ \ ] = \frac{n}{V}$ where $V = 1dm^3$

$[SOCl_2] = 0.2M$

$[SO] = 0.4M$

$[Cl_2] = 2M$

$$Q_c = \frac{[SO][Cl_2]}{[SOCl_2]} = \frac{0.4M \times 2M}{0.2M} = 4M$$

But $K_c = 1.2M$. So $Q_c > K_c$ and hence the reaction will proceed in reverse direction to establish the equilibrium**.**

$$SOCl_{2(g)} \rightleftharpoons SO_{(g)} + Cl_{2(g)}$$

	$SOCl_2$	SO	Cl_2
Initially	0.2	0.4	2
At equilibrium:	$0.2 + x$	$0.4 - x$	$2 - x$

$$K_c = \frac{[SO][Cl_2]}{[SOCl_2]}$$

Then $\frac{(0.4-x)(2-x)}{(0.2+x)} = 1.2$

At equilibrium $n_T = (0.2 + x) + (0.4 - x) + (2 - x) = 2.437$moles

Number of moles of $SOCl_2 = 0.2 + x = 0.363$ moles

Number of moles of $SO = 0.4 - x = 0.237$ moles

Number of moles of $Cl_2 = (2 - x) = 1.837$ moles

$$\%SOCl_2 = \frac{n_{SOCl_2}}{n_T} \times 100\% = \frac{0.363}{2.437} \times 100\% = 14.9\%$$

$$\%SO = \frac{n_{SO}}{n_T} \times 100\% = \frac{0.237}{2.437} \times 100\% = 9.7\%$$

$$\%Cl_2 = \frac{n_{Cl_2}}{n_T} \times 100\% = \frac{1.837}{2.437} \times 100\% = 75.4\%$$

Hence the equilibrium composition of each gas is 14.9%, 97% and 75.4% by volume for $SOCl_2$, SO, and Cl_2 respectively.

Question 42

(a) Is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction. It is the state in which both reactants and products are simultaneously consumed and produced by the same speed such that their concentrations remain unchanged.

(b) Conditions which favour the formation of chemical equilibrium are:
- The system (reaction) must be reversible.
- The reaction should take place in a closed system, that is; no material is allowed to enter or to leave the system.

(c) $$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initially	1	1	0	0
At equilibrium	$1 - x$	$1 - x$	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(^x/_V)(^x/_V)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)}$$

$$K_c = \frac{x^2}{x^2 - 2x + 1}$$

But $1 - x = {}^1/_3$ or $x = {}^2/_3$ (One third of ethanoic acid remains at equilibrium).

Substituting $x = {}^2/_3$ in above equilibrium constant expression gives, $K_c = 4$.

If three quarters of one mole of ethanol is used:

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

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initially	1	$^3/_4$	0	0
At equilibrium	$1 - x$	$^3/_4 - x$	x	x

$$K_c = \frac{(^x/_V)(^x/_V)}{\left(\frac{^3/_4 - x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 1.75x + 0.75} = 4 \quad \text{or } x = 0.57$$

And $1 - x = 1 - 0.57 = 0.43$ moles

Hence the amount of ethanoic acid which would remain is 0.43moles.

Question 43

(a)

(i) Yellow colouration of CrO_4^{2-}.
(Addition of NaOH is equivalent to removal of H^+ thus shifting the position of equilibrium to the right).

(ii) Orange colouration of $Cr_2O_7^{2-}$ (Addition of HCl(aq) shift the position of chemical equilibrium to the left).

(iii) Orange colouration of $Cr_2O_7^{2-}$ (Anhydrous $CaCl_2$ absorbs thus shifting position of chemical equilibrium to the left).

(b)

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

	$N_2O_{4(g)}$	$2NO_{2(g)}$
Initially	1	0
At equilibrium	$1 - \alpha$	2α

Where α is numerically equal to the degree of dissociation.

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(X_{NO_2}P_T)^2}{(X_{N_2O_4}P_T)} = \frac{(X_{NO_2})^2 P_T}{(X_{N_2O_4})}$$

But $X_{NO_2} = \frac{2\alpha}{1+\alpha}$ Where $n_T = (1 - \alpha) + 2\alpha = 1 + \alpha$

And $X_{N_2O_4} = \frac{1-\alpha}{1+\alpha}$

Then $K_p = \frac{4\alpha^2 P_T}{1-\alpha^2}$

When $\alpha = 0.5$ and $P_T = 1atm$

$$K_p = \frac{4 \times 0.5^2 \times 1}{1 - 0.5^2} atm = {}^4/_3 \text{ atm}$$

Hence the equilibrium constant in terms of pressure is $^4/_3$ atm

When the pressure, P_T is changed to 10atm

From $K_p = \frac{4\alpha^2 P_T}{1-\alpha^2}$

When $P_T = 10\text{atm}$

Since temperature is kept constant, K_p remain unchanged.

Then $^4/_3 = \frac{4\times10\alpha^2}{1-\alpha^2}$ or $\alpha = 0.18$ or 18%

Hence when the pressure is 10atm, degree of dissociation of the gas becomes 18%.

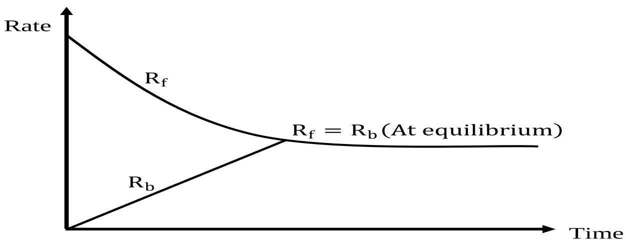
Question 44

(a)

(i) Chemical equilibrium involves balance of the rate of the two reactions which are **proceeding at the same time** in **opposite directions.** So it involves the **constant interchange of particles in motion,** moving in opposite direction of forward and reverse reaction and hence the equilibrium is said to be dynamic.

(ii) Consider the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Initially the rate of forming HI (forward reaction) is maximum while that of dissociation of HI to form H_2 and I_2 (backward reaction) is zero because at the beginning, only H_2 and I_2 are present. As the reaction proceed concentration of H_2 and I_2 start to decrease and thus lowering the rate of forward reaction while HI is formed leading to backward reaction. Thus as the reaction proceed, the rate of forming HI is continuously decreasing while that of dissociation of HI is continuously increasing until they become equal where it said that the equilibrium has been attained as illustrated in the following graph:



Where:

R_f is the rate of formation of HI (forward reaction rate)

R_b is the rate of dissociation of HI (backward reaction)

(b) Equation for the reaction: $I_2 \rightleftharpoons I + I$

Simplified equation after combining two I atoms is;

	I_2	$\rightleftharpoons$	$2I$
Initially	1		0
At equilibrium	$1-\alpha$		2α

$$K_p = \frac{(P_I)^2}{(P_{I_2})} = \frac{(X_I P_T)^2}{(X_{I_2} P_T)} = \frac{(X_I)^2 P_T}{(X_{I_2})}$$

$$X_I = \frac{2\alpha}{1+\alpha} \quad \text{and} \quad X_{I_2} = \frac{1-\alpha}{1+\alpha}$$

Then $K_p = \frac{4\alpha^2 P_T}{1-\alpha^2}$ But $\frac{2\alpha}{1+\alpha} = 0.4$ (iodine vapour contains 40% by volume of iodine atoms) or $\alpha = 0.25$

And it is given that $P_T = 1\text{atm}$

$$K_p = \frac{4\times0.25^2\times1}{1-0.25^2} = \frac{4}{15}\text{atm}$$

If the pressure is reduced to 20%

$\frac{2\alpha}{1+\alpha} = 0.2$ or $\alpha = \frac{1}{9}$

Substituting $\alpha = \frac{1}{9}$ and $K_p = \frac{4}{15}$

$$\frac{4}{15} = \frac{4\left(\frac{1}{9}\right)^2 P_T}{1-\left(\frac{1}{9}\right)^2} \quad \text{or} \quad P_T = 5.33\text{atm}$$

Thus the percentage will be reduced to the given amount when the total pressure is 5.33atm.

Question 45

(a) The value of equilibrium constant for the titration reaction is infinitely large.

(b)

	$N_{2(g)}$ +	$O_{2(g)}$ ⇌	$2NO_{(g)}$
Initially	1	1	0
At equilibrium	$1-\alpha$	$1-\alpha$	2α

$$K_p = \frac{(P_{NO})^2}{(P_{O_2})(P_{N_2})} = \frac{(X_{NO}P_T)^2}{(X_{O_2}P_T)(X_{N_2}P_T)} = \frac{(X_{NO})^2}{(X_{O_2})(X_{N_2})}$$

But $n_T = (1-\alpha) + (1-\alpha) + 2\alpha = 2$ moles

Then $X_{NO} = \frac{2\alpha}{2} = \alpha$

$$X_{N_2} = X_{O_2} = \frac{1-\alpha}{2}$$

So $3.6 \times 10^{-3} = \frac{4\alpha^2}{(1-\alpha)^2} = \frac{4\alpha^2}{\alpha^2-2\alpha+1}$

Or $3.9964\alpha^2 - 0.0072\alpha - 0.0036 = 0$ or $\alpha = 0.029$

Hence the fraction of original nitrogen which is used in the reaction is 0.029

The fraction by volume of nitric oxide in the mixture $= X_{NO} = \alpha = 0.029$

Hence the fraction of nitric oxide in the mixture is also 0.029

Question 46

(a) No. For the equilibrium to be achieved, reaction rates (not rate constant) for forward and reverse reactions must be the same. Rate constants for forward and reverse reactions are different and they are not changing in the course of chemical reaction.

(b) $X_{PCl_3} = X_{Cl_2} = 0.407$ (Both PCl_3 and Cl_2 are produced from the decomposition of the phosphorous pentachloride introduced in the vessel and their mole ratio is 1:1).

$X_{PCl_3} + X_{Cl_2} + X_{PCl_5} = 1$

Thus; $X_{PCl_5} = 1 - (X_{Cl_2} + X_{PCl_3}) = 1 - (0.407 + 0.407) = 0.186$

Using; $P' = XP_T$

Partial pressure of PCl_3, $P_{PCl_3} = 0.407 \times 202\text{kPa} = 82.214\text{kPa}$

Partial pressure of PCl_5, $P_{PCl_5} = 0.186 \times 202\text{kPa} = 37.572\text{kPa}$

$P_{PCl_3} = P_{Cl_2} = 82.214\text{kPa}$ (They have the same mole fraction)

$$K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{82.214\text{kPa} \times 82.214\text{kPa}}{37.572\text{kPa}} = 179.9\text{kPa}$$

Question 47

(a)

(i) At the beginning of the chemical reaction where there are only reactants (with zero amount of products).

(ii) At the completion of the chemical reaction whereby all reactants have been converted to products.

(b)

	CO_2 +	H_2 ⇌	CO +	H_2O
At equilibrium	$0.45-x$	$0.45-x$	x	x

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{x^2}{(0.45-x)} = 0.11$$

Solving above equation gives $x = 0.11$

Hence at equilibrium:

Numbers of moles CO_2 = Number of moles of $H_2 = 0.45 - x = 0.34$moles

Number of moles of CO = Number of moles of $H_2O = x = 0.11$moles

Addition of CO_2 and H_2 will shift the position of equilibrium to the right so as to re – establish the equilibrium:

	CO_2 +	H_2 ⇌	CO +	H_2O
Just after the addition	0.68	0.68	0.11	0.11
At new equilibrium	$0.68-x$	$0.68-x$	$0.11+x$	$0.11+x$

Then $0.11 = \frac{(0.11+x)^2}{(0.68-x)^2}$ or $x = 0.0869$

From which x = 0.0869

Hence at new equilibrium:

Number of moles of CO_2 = Number of moles of H_2 = $0.68 - x = 0.5931$moles

Number of moles of CO = Number of moles of H_2O = $0.11 + x = 0.1969$moles

Question 48

(a) Given that:

$H_2(g) + I_2(g) \rightleftharpoons 2HI_{(g)}; K_{P1} = 54$ …………………….. (i)

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ K_{P2} = 1.04 \times 10^{-4}$ …….. (ii)

Taking 3 × (i) gives:

$3H_2(g) + 3I_2(g) \rightleftharpoons 6HI_{(g)};\ K_{P3} = (K_{P1})^3$……………. (iii)

Reversing (ii) gives;

$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g);\ K_{P4} = \frac{1}{K_{P2}}$ ………….... (iv)

Taking (iii) + (iv) gives the required equation which is:

$2NH_3(g) + 3I_2(g) + \cancel{3H_2(g)} \rightleftharpoons 6HI_{(g)} + N_2(g) + \cancel{3H_2(g)}$

Or $2NH_3(g) + 3I_2(g) \rightleftharpoons 6HI(g) \quad + N_2(g); K_P = K_{P3} \times K_{P4}$

Thus the required $K_P = (K_{P1})^3 \times \frac{1}{K_{P2}} = 54^3 \times \frac{1}{1.04\times10^{-4}} = 1.51 \times 10^9$

The value of K_P is 1.51×10^9

(b)

	$N_2(g)$	$+ 3H_2(g)$	$\rightleftharpoons 2NH_3(g)$
Initially	1	3	0
At equilibrium	$1 - x$	$3 - 3x$	$2x$

$n_T = (1 - x) + (3 - 3x) + 2x = 4 - 2x$

But $\left(\frac{2x}{4-2x}\right) \times 100 = 1.2$ (molar percent of NH_3 is 1.2)

From which $x = 0.024$moles

At equilibrium:

Number of moles of $N_2 = 1 - x = 0.97$moles

Number of moles of moles of $H_2 = 3 - 3x = 2.928$moles

Number of moles of $NH_3 = 2x = 0.048$moles

Total number of moles, $n_T = 4 - 2x = 3.952$moles

$$P_{NH_3} = X_{NH_3}P_T = \frac{0.048 \times 10\text{atm}}{3.952} = 0.12\text{atm}$$

$$P_{H_2} = X_{H_2}P_T = \frac{2.928 \times 10\text{atm}}{3.952} = 7.4\text{atm}$$

$$P_{N_2} = X_{N_2}P_T = \frac{0.976 \times 10\text{atm}}{3.952} = 2.47\text{atm}$$

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{0.12^2}{2.47 \times 7.4^3} = 1.44 \times 10^{-5}\text{atm}^{-2}$$

Hence K_p for the reaction is $1.44 \times 10^{-5}\text{atm}^{-2}$

Molar percent of NH_3 is 10.4

Then $\left(\frac{2x}{4-2x}\right) \times 100 = 10.4$

From which $x = 0.188$

Then at new equilibrium:

Number of moles of $N_2 = 1 - x = 0.812$moles

Number of moles of $H_2 = 3 - 3x = 2.436$ moles

Number of moles of $NH_3 = 2x = 0.376$moles

Total number of moles, $n_T = 4 - 2x = 3.624$ moles

$$P_{NH_3} = X_{NH_3}P_T = \frac{0.376P_T}{3.624} = 0.1P_T$$

$$P_{H_2} = X_{H_2}P_T = \frac{2.436\ P_T}{3.624} = 0.672P_T$$

$$P_{N_2} = X_{N_2}P_T = \frac{0.812P_T}{3.624} = 0.224P_T$$

$$K_P = \frac{(0.1P_T)^2}{(0.224P_T)(0.672P_T)^3} = \frac{0.147}{(P_T)^2} = 1.44 \times 10^{-5}; \quad P_T = 101\text{atm}$$

Thus the required pressure for molar percent of NH_3 to be 10.4 is 101atm.

Question 49

(a) No. At equilibrium, concentrations of products and reactants do not change; this does not mean they are equal. The equality exists in the reaction rate of forward and reverse reaction; this also does not mean equal concentration of reactants and products due to difference of rate constants and reaction orders (for forward and reverse reactions).

(b) Let required number of moles of NH_3 be a

Then:

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initially	0		0		0
At equilibrium	x		3x		a − 2x

But at equilibrium $[H_2] = 6M$

Thus $3x = 6$ or $x = 2$

Hence concentration of each at equilibrium is as follows:

$[NH_3] = a - 2x = (a-4)M$, $[N_2] = x = 2M$ and $[H_2] = 6M$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(a-4)^2}{(2)\times(6)^3}$$

Or $a - 4 = \sqrt{(1.8)\times(2)\times(6)^3} = 27.9$ or $a = 31.9$ moles

Hence 31.9 moles of ammonia must be places in 1 litre container.

Question 50

(a) In the open container, carbon dioxide (another product of the decomposition) being a gas escapes to atmosphere, leaving the system and therefore the reverse reaction (between carbon dioxide and calcium oxide) will not occur. Consequently, the decomposition will continue until there is zero amount calcium carbonate in the container.

(b) From the given reaction equation: $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

If number of moles $SO_2 =$ number of moles of SO_3;

Then $[SO_2] = [SO_3]$ and $K_c = \frac{1}{[O_2]}$

$[O_2] = \frac{1}{K_c} = \frac{1}{100} = 0.01M$;

Then using $n = V[\quad]$;

Number of moles in 10L flask $= 10 \times 0.01$ moles $= 0.1$moles

Hence 0.1moles of O_2 present in the flask

If number of moles of $SO_3 = 2\times$ number of moles of SO_2

Then $2[SO_2] = [SO_3]$

So $K_c = \frac{(2[SO_2])^2}{[SO_2]^2[O_2]} = \frac{4}{[O_2]}$

$$[O_2] = \frac{4}{K_c} = \frac{4}{100} = 0.04$$

Thus number of moles of O_2 in 10L flask $= 10 \times 0.04$moles $= 0.4$moles

Hence 0.4 moles of O_2 present in the flask.

Question 51

(a) Reaction quotient is obtained from concentration of reactants and products at any time in the reaction course and therefore it may take any value from zero (when concentrations of reactants are non-zero while those of products are zero; at the beginning of chemical reaction) to infinitely large (when concentrations of reactants are zero while those of products are non-zero; at the completion of chemical reaction). This is different to equilibrium constant which is obtained at a particular time in the reaction course when the equilibrium has been achieved; that is, its value is specific for concentration of reactants and products at equilibrium only.

(b) Calculating the value of reaction quotient to know the reaction direction:

$$Q_c = \frac{[H_2][F_2]}{HF^2} = \frac{\left(\frac{0.5}{V}\right)\left(\frac{0.75}{V}\right)}{\left({}^{5}/_{V}\right)^2} = 0.015 = 1.5\times10^{-2}$$

But the given K_c value is 1×10^{-2}which is smeller than the reaction quotient (1.5×10^{-2})

Since $Q_c > K_c$, the reaction will proceed in reverse direction to establish the equilibrium.

	$2HF_{(g)} \rightleftharpoons$	$H_{2(g)} +$	$F_{2(g)}$
Initial (At t = 0)	5	0.5	0.75
At equilibrium	$5 + x$	$0.5 - x$	$0.75 - x$

$$K_c = \frac{[H_2][F_2]}{HF^2} = \frac{\left(\frac{0.5 - x}{V}\right)\left(\frac{0.75 - x}{V}\right)}{\left(\frac{5 + x}{V}\right)^2}$$

Then;

$$1 \times 10^{-2} = \frac{x^2 - 1.25x + 0.375}{x^2 + 10x + 25}$$

From which; $0.99x^2 - 1.35x + 0.125 = 0; x = 0.1$

Hence:

$$[HF] = \frac{5 + x}{V} = \frac{(5 + 0.1)\text{mol}}{5L} = 1.02M$$

$$[H_2] = \frac{0.5 - x}{V} = \frac{[0.5 - 0.1]\text{mol}}{5L} = 0.08\ M$$

$$[F_2] = \frac{0.75 - x}{V} = \frac{[0.75 - 0.1]\text{mol}}{5L} = 0.13M$$

Question 52

(a) Agree

Explanation:

Equilibrium constant determines relative concentration of products to that of reactants at equilibrium whereby very large value of equilibrium constant implies that equilibrium concentrations of products are high compared to equilibrium concentrations of reactants and vice-versa. On another hand if the equilibrium constant is close to 1 means that equilibrium concentrations of reactants and products do not differ much.

(b) For gases, pressure ratio = mole ratio.

So, if initially was only solid ammonium carbamate in the vessel, at the first equilibrium; $P_{NH_3} = 2P_{CO_2}$

Thus if we let $P_{CO_2} = P$, then $P_{NH_3} = 2P$

And if P_{CO_2} at new equilibrium is P'

Then P_{NH_3} at new equilibrium will be P'' (Not $2P'$ because after the addition of ammonia the mole ratio is disturbed).

But P_{NH_3} at new equilibrium $=$ Total pressure in the first equilibrium

$= P + 2P = 3P$

Thus $P'' = 3P$ or $P'' = \frac{3}{2}P$

	$NH_2COONH_4(s) \rightleftharpoons$	$2NH_3(g) +$	$CO_2(g)$
At the first equilibrium		2P	P
At the final equilibrium		3P	P′

$$K_p = \left(P_{NH_3}\right)^2 \times P_{CO_2} = (2P)^2 \times P = (3P)^2 \times P'$$

From which $P' = \frac{4}{9}P$

Original total pressure $= 2P + P = 3P$

Final total pressure $= 3P + P'$

$$\frac{\text{Final total pressure}}{\text{Original total pressure}} = \frac{3P + P'}{3P} = \frac{3P + \frac{4}{9}P}{3P} = \frac{31}{27}$$

Hence the ratio is $\frac{31}{27}$.