Suggested Answers

Paper 1

Section A

1 (a)

We can use the successive ionization enthalpies of silicon to prove the electronic arrangement of silicon.

(1 mark)

The removal of electrons from a completely filled electron shell will result in a sudden increase in ionization enthalpy. The 5th ionization enthalpy and the 13th ionization enthalpy are significantly higher than the 4th and the 12th ionization enthalpy respectively. This indicates that the 5th electron and the 13th electron are located in a completely filled electron shell. Hence the electronic arrangement of silicon should be (2, 8, 4).

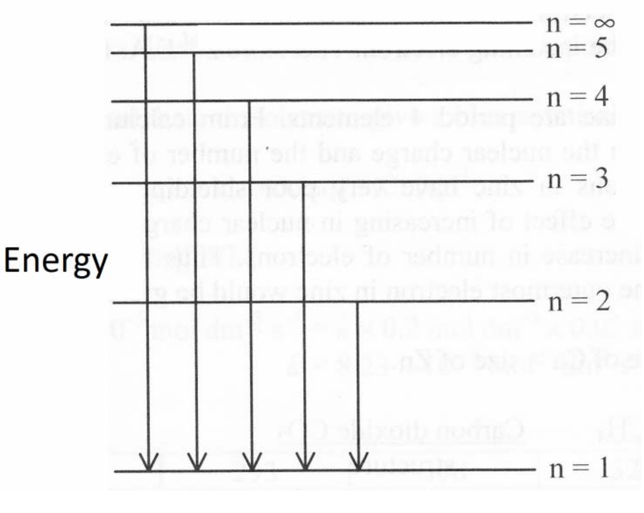
(2 marks)

1 (b)

(i) The spectral lines represent the electron transitions from higher energy levels to lower energy levels in a hydrogen atom.

(1 mark)

(ii) As seen in the diagram, the energy difference between energy levels reduces with increase in principal quantum number n.



(2 marks)

(iii) Let the frequency of the convergence limit of the series be $v_{\infty \text{ to } 1}$

By Planck equation: $E = hv_{\infty \text{ to } 1}$

This amount of energy is equivalent to the energy needed to ionize 1 hydrogen atom.

Thus, I. E. = Avogadro's number × E

(3 marks)

(iv) It can be used to identify what element is present in a sample.

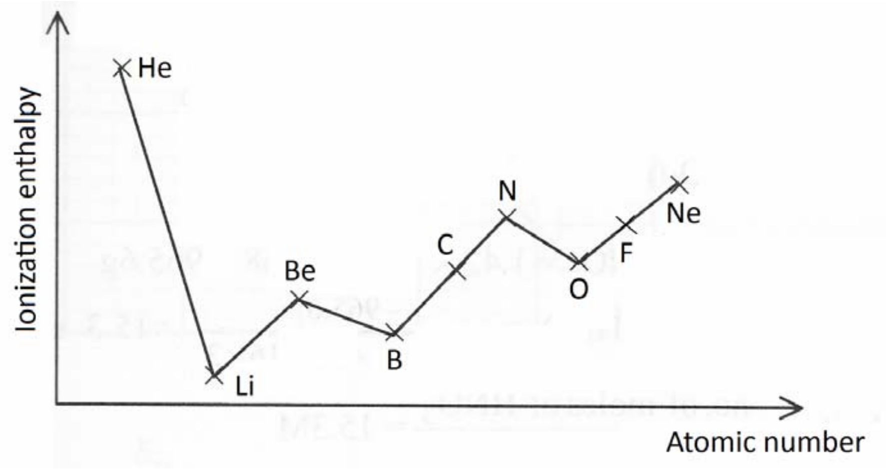
(1 marks)

2 (a)

(i) The first ionization enthalpy of an element is the enthalpy change when 1 mole of electrons is removed from 1 mole of gaseous atoms of the element under standard conditions.

(1 mark)

(ii)



(3 marks)

2 (b)

$$H_2NNH_2(g) + 2\,F_2(g) \rightarrow N_2(g) + 4\,HF(g) \qquad (1)$$

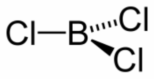
$$\begin{aligned}\Delta H &= -E(N{\equiv}N) - 4\,E(H{-}F) + 4\,E(N{-}H) + E(N{-}N) + 2\,E(F{-}F)\\ &= -945 - 4\,(565) + 4\,(390) + 163 + 2\,(158)\\ &= \underline{\underline{-1166\text{ kJ mol}^{-1}}}\end{aligned}$$

$$H_2NNH_2(g) + O_2(g) \rightarrow N_2(g) + 2\,H_2O(g) \qquad (2)$$

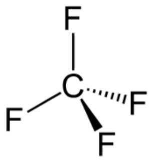
$$\begin{aligned}\Delta H &= -E(N{\equiv}N) - 4\,E(O{-}H) + 4\,E(N{-}H) + E(N{-}N) + E(O{=}O)\\ &= -945 - 4\,(464) + 4\,(390) + 163 + 498\\ &= \underline{\underline{-580\text{ kJ mol}^{-1}}}\end{aligned}$$

3 (a)

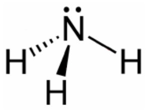
(i) BCl_3 Trigonal planar



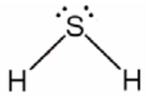
(ii) CF_4 Tetrahedral



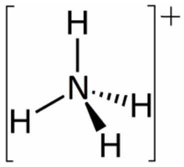
(iii) NH_3 Trigonal pyramidal



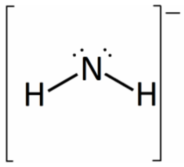
(iv) H_2S V-shaped



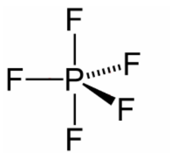
(v) NH_4^+ Tetrahedral



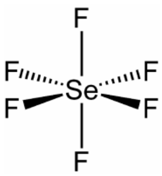
(vi) NH_2^- V-shaped



(vii) PF_5 Trigonal bipyramidal



(viii) SeF_6 Octahedral



3 (b)

(i) Boiling point of a substance mainly depends on the strength of intermolecular forces. In H_2O, there are 2 hydrogen bonds formed in each molecule. There is only one hydrogen bond formed in each CH_3OH molecule, while CH_3OCH_3 cannot form hydrogen bonds among molecules (only van der Waals force is present). Thus, strength of intermolecular force in descending order is:

$$CH_3OCH_3 < CH_3OH < H_2O$$

And boiling point:

$$CH_3OCH_3 < CH_3OH < H_2O$$

(ii) The main molecular attraction in the 3 species is van der Waals forces. The strength of van der Waals forces depends on the size of electron cloud of the molecules. As size of $CH_3SCH_3 > CH_3SH > H_2S$, strength of intermolecular forces:

$$CH_3SCH_3 > CH_3SH > H_2S$$

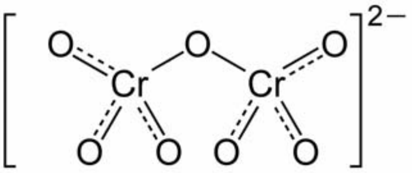
Thus, the boiling point of the series is in the above order.

(3 marks)

4 (a) (i)

(1) Cr : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

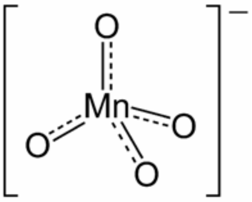
(2) The structure for the dichromate(VI) ion:



4 (a) (ii)

(1) Mn : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

(2) The structure for the permanganate(VII) ion:



(3 marks)

4 (b)

Potassium and copper are Period 4 elements. From potassium to copper, there is an increase in both the nuclear charge and the number of electrons. However, the extra 3d electrons in copper have very poor shielding effect on outermost 4s electrons. So the effect of increasing in nuclear charge outweighs the shielding effect of the increase in number of electrons. Thus the attraction between the nucleus and the outermost electron in copper would be greater than that in potassium.

Thus, size of K > size of Cu.

(2 marks)

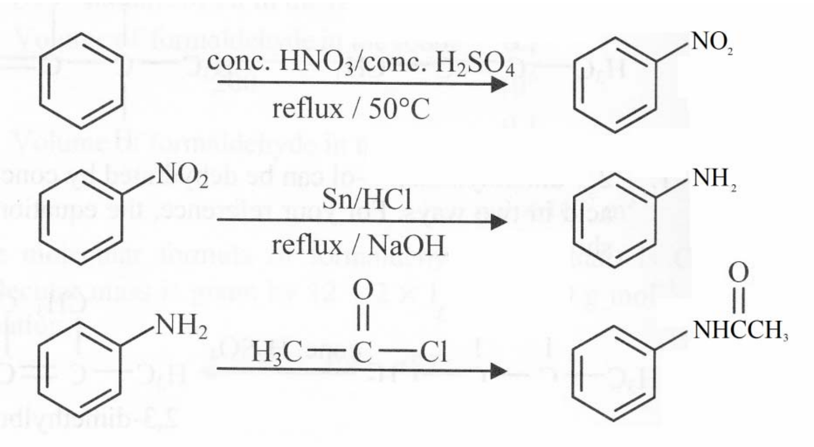
5 (a)

(i) B
(ii) A
(iii) C
(iv) D

(4 marks)

5 (b)

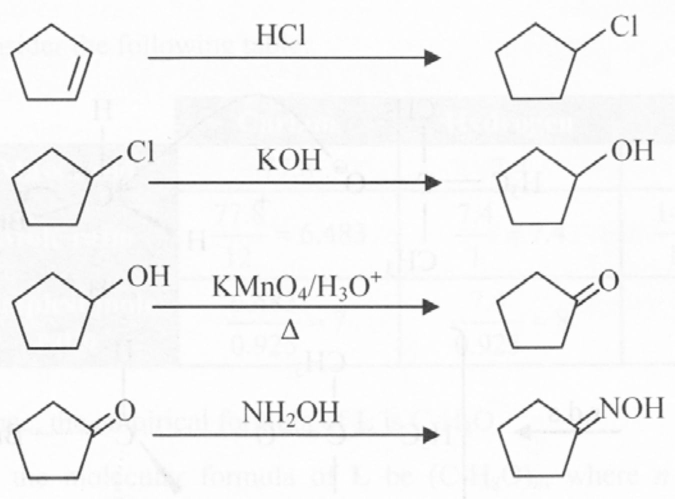
(i)



(3 marks)

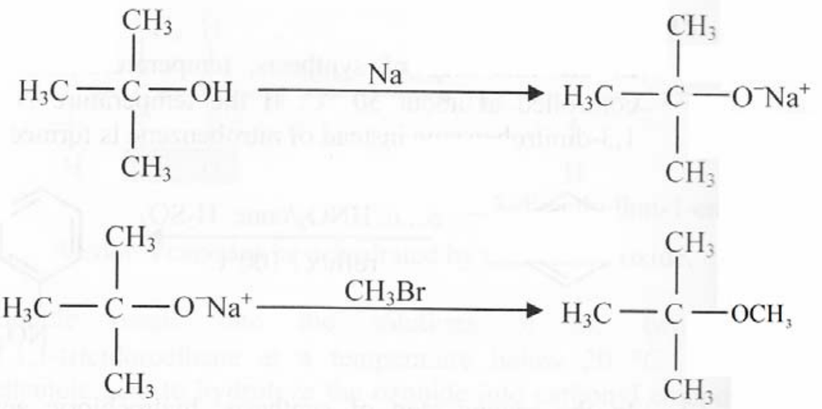
5 (b)

(ii)

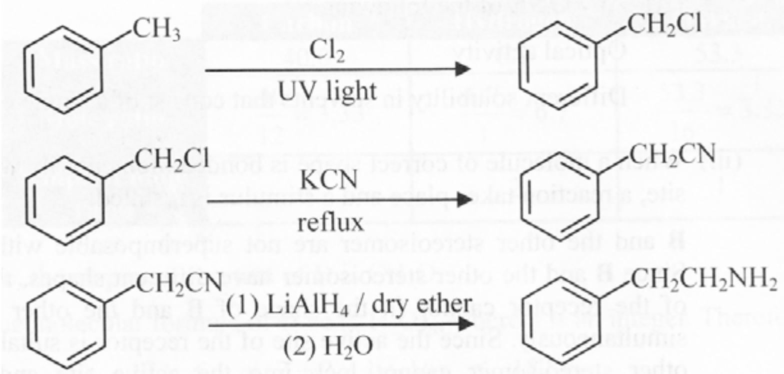


(3 marks)

(iii)

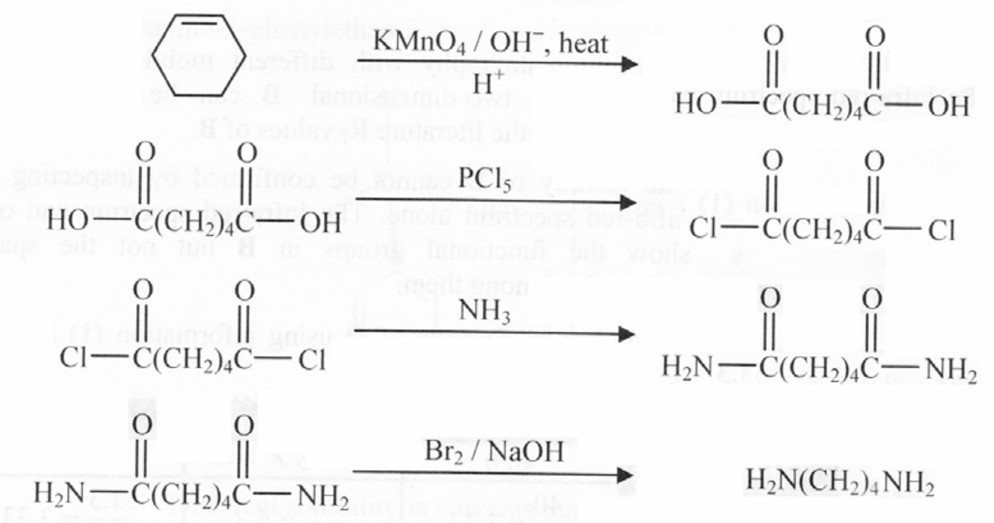


6 (a)



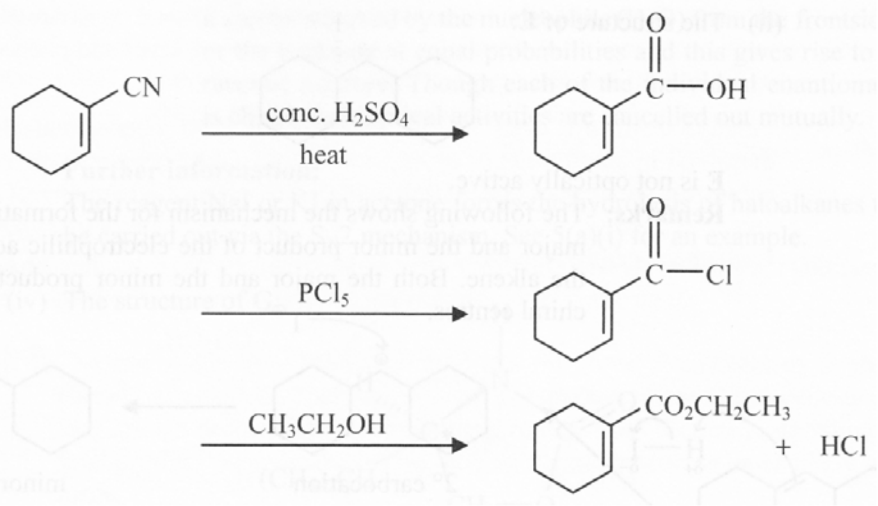
(5 marks)

6 (b)



(3 marks)

6 (c)



(3 marks)

Section B

7

Step 1: A standard KOH(aq) should not be prepared using the method as described.

Explanation: KOH(s) is hydroscopic.

Correction: It is necessary to standardize KOH(aq) before use.

(3 marks)

Step 3: The burette should not be rinsed with water only.

Explanation: Water that remains in the burette will cause a dilution of the KOH(aq).

Correction: The burette needs to be rinsed with distilled water and then with the KOH(aq) prepared.

(3 marks)

Step 4: Methyl orange is not a suitable indicator.

Explanation: The experiment involves a titration of a weak acid with a strond alkali. pH at the end point is about 8 to 9.

Correction: Phenolphthalein should be used.

(3 marks)

Step 5: Calculation should not be based on the result of one titration only.

Explanation: There may be errors in the titration.

Correction: Repeat the titration at least 3 times. Use the mean titre for the calculation.

(3 marks)

8 (a)

(1) All living things have a constant proportion of ^{14}C.

However, when organisms died, replacement of ^{14}C ceases while decay of ^{14}C continues.

By comparing the content of ^{14}C in fossil specimens with the living things nowadays, it is possible to estimate the age of specimens.

(2 marks)

(2) Since the half life for the decay of carbon-14 = 5730 years,

$$t_{½} = \frac{\ln 2}{k}$$

$$5730 = \frac{\ln 2}{k}$$

$$k = 1.21 \times 10^{-4} \text{ year}^{-1}$$

$$\ln 8.5 = -(1.21 \times 10^{-4})\,t + \ln 15.3$$

$$t = \underline{\underline{4858 \text{ years}}}$$

(3 marks)

8 (b)

Conduct experiments several times at different temperatures.
Different rate constants (k) are determined at different temperatures respectively.

By plotting ln k vs $\frac{1}{T}$, a straight line is obtained with slope = – $\frac{E_a}{R}$

Thus, the activation energy (E_a) can be determined.

(3 marks)

Section C

9

A buffer solution resists pH changes when small amounts of acid or alkali is added to it. It plays an important role in chemical processes which require a fairly constant pH environment. Buffer could be classified into acidic buffer and basic buffer.

Acidic buffer

An acidic buffer has a pH less than 7. They are made from a weak acid and its salt. A typical example is the mixture of ethanoic acid and sodium ethanoate solutions. pH of buffer solutions could be adjusted by changing the ratio of acid and salt, or by choosing a different acid and the corresponding salt.

Ethanoic acid is a weak acid and the equilibrium position in the following equation will lie more on the L.H.S.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Adding sodium ethanoate to ethanoic acid solution will shift the equilibrium position even further to the left, in accordance to Le Chatelier Principle.

Effect of small amount of acid on acidic buffer

If a small amount of strong acid (e.g. HCl) is added to acidic buffer, most of the added hydroxonium ions are removed by ethanoate ions to form ethanoic acid. Since ethanoic acid is a weak acid, the equilibrium is well to the right:

$$CH_3COO^- + H_3O^+ \rightleftharpoons CH_3COOH + H_2O$$

In this way, most of the hydroxonium ions are removed by ethanoate ions, and thus the pH of solution is not altered to a great degree.

Effect of small amount of alkali on acidic buffer

When a strong base (e.g. NaOH) is added to acidic buffer, ethanoic acid reacts with it and consumes the excess OH^- ions:

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

Thus, H_3O^+ ions present in the acid buffer will not be consumed by the added alkali. Since the incoming OH^- ions are removed, the pH remains almost constant.

Basic buffer

A basic buffer has a pH higher than 7. They are made from a weak alkali and its salt. A mixture of ammonia and ammonium chloride solutions is a typical example.

Ammonia is a weak base and the equilibrium position of the following equation will lie more on the L.H.S.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Adding ammonium chloride to this ammonia solution will shift the equilibrium position even further to the left, in accordance to Le Chatelier Principle.

Effect of small amount of acid on basic buffer

When a strong acid (e.g. HCl) is added to basic buffer, ammonia reacts with it and consumes the excess H_3O^+ ions:

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

Since most of the incoming H_3O^+ ions are removed, and the pH will not decrease significantly.

Effect of small amount of alkali on basic buffer

When a strong alkali is added to this buffer, the incoming hydroxide ions are removed by a simple reaction with ammonium ions:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

In this way, most of the hydroxide ions are removed from the solution. Thus, H_3O^+ ions present in the basic buffer will not be consumed by the incoming OH^- ions and the pH of solution will not change very much.

Applications of buffer in our daily life

In laboratory, buffers are useful in preparing solution of a known and constant pH for checking the indicators and calibrating pH meters. They are used to control the pH of reaction mixtures in chemical and biochemical reactions. Moreover, buffers are also used as food preservatives to limit the acidity of food.

In many industrial and physiological processes, reactions usually take place at optimum pH values. When the pH values vary, undesirable reactions and effects may occur.

For example, the pH of our blood lies at about 7.35. If this value drops below or rises above 7.0, the results are fatal. Fortunately, our blood contains a buffering system which maintains the pH at the proper level. Plasma protein molecules act as buffers as they bear both the carboxylic acid group (–COOH) and the basic amino group ($-NH_2$).

$$H_2O + CO_2 \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

The protein acts as a base which neutralizes the additional H^+ ions formed at high concentration of CO_2. Meanwhile, it can also function as an acid to remove the additional HCO_3^- ions. Hence, a fairly constant pH of blood is maintained.

Conclusion

A solution of stable pH is always important in many chemical and biochemical processes and is achieved by the presence of buffer. Particularly, buffer solutions are important to human body: without the protection provided by the buffering system, we could not eat and adsorb acidic or basic foods.

10

Chemical kinetics is the studies of the rates of chemical reactions and the factors affecting them. A brief review on these factors and the applications of chemical kinetics will be presented below.

Temperature

Reactions go faster when is the reactants are heated. Reactant particles are moving at different velocities and there are high-energy collisions (effective collision) and low-energy collisions between them. Only a small fraction of particles having the activation energy (E_a) will collide with each other to form products. An increase in temperature will increase the number of reactant particles having E_a, thus leading to effective collisions and producing more products.

In fact, the fraction of effective collisions increases exponentially with temperature, as shown by the Arrhenius equation:

$$k = Ae^{-\frac{Ea}{RT}}$$

where k is the rate constant of the reaction, A is Arrhenius constant, R is the ideal gas constant and T is the temperature of reaction mixture.

Concentration

Many chemical reactions take place in solution. The concentration of reactant may affect the speed of reaction. According to the Collision Theory, frequency of collisions increases with increasing concentration and higher collision frequency will lead to a higher chance of effective collisions. Thus, the reaction rate generally increases with the concentration of reactants.

Pressure

For gaseous reactions, increase in pressure usually speed up the reaction rate. If the pressure of the gases is increased by compression, molecules are pushed closer together. Consequently, the concentration of gases increases and the molecules collide more frequently and react more rapidly. Thus, the rate of gaseous reaction increases. However, we should notice that pressure has little effect on the reaction involving solids and liquids because of their incompressibility.

Surface area for reaction

When the reactant involves a solid, the surface area of solid reactants will affect the reaction rate. Thus, in order to speed up the reaction powdered reactants are usually used. The greater the surface area in contact for reactant particles, the higher is the reaction rate.

Light

Light is another form of energy that speeds up some chemical reactions. A typical example is photosynthesis in which green plants synthesize sugars under sunlight. Moreover, the formation of silver salts during the exposure of photographic films to light also speeds up by higher light intensity.

Catalyst

A catalyst is a substance which increases the speed of chemical reaction without being used up in the reaction. It speeds up the reaction by providing a new mechanism with lower E_a for the reaction. Thus, more molecules can react at a given temperature.

Uses of chemical kinetics

The principles of chemical kinetics play an important role in the design and optimizing working conditions of industrial processes. In order to achieve fast chemical conversions of reactants into products with high yield, the reaction conditions (e.g. temperature, pressure, catalyst) should be carefully chosen.

However, it is sometimes important to reduce the reactions rate in some cases. For example, food preservatives are added to canned food to slow down the deterioration rate. The rates of corrosion and rusting have always been the concern of society. These undesirable reactions are costly not only because of the need to protect metal objects, but also the expenses involved in the replacement of corroded articles. In archaeology, carbon-14 dating is widely used in dating the age of fossils and ancient biological specimens.

Chemical kinetics also provides invaluable information for the understanding of reaction mechanism. By considering the order of reaction with respect to different reactants, the detailed sequence of bond breaking and rearrangement of atoms during a reaction can be speculated.

For example, kinetic studies show that in the following reaction:

$$CH_3CH_2CH_2Br + H_2O \rightarrow CH_3CH_2CH_2OH + Br^-$$

Rate = $k[CH_3CH_2CH_2Br][OH^-]$. To satisfy with this rate equation, a mechanism with both $CH_3CH_2CH_2Br$ and OH^- involving in the rate determining step should be involved. It leads to the fact that this reaction is described as bimolecular nucleophilic substitution (S_N2).

Conclusion

Kinetic studies and the theories of chemical equilibrium (e.g. Le Chatelier Principle) build up a strong theoretical ground in the optimization of industrial production of chemicals as well as in the fundamental research on the mechanism of chemical reactions.