

## KINETIC STUDY OF METHYL BROMIDE PRODUCTION

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## ABSTRACT

The kinetics of methyl bromide production from methanol and hydrobromic acid is studied. This study has shown that the reaction is second order. The catalyst concentration dependence of reaction rate constant is investigated. The reaction rate constant increased from 0.0107 to 0.0160 by increasing the catalyst concentration from 0 to 1.494 mol/l at 60 °C and from 0.0207 to 0.0246 at 70 °C respectively.

The activation energy is calculated at different catalyst concentrations. The value of activation energy decreased from 6.28 to 4.85 kJ/mol by increasing the catalyst concentration from zero to 1.494 mol/l respectively.

## INTRODUCTION

Methyl bromide has been employed extensively in agriculture as a toxic fumigant to control the pests of the stored grain, plant and various soil<sup>(1)</sup>. It is suitable for fumigation of food commodities and establishments in which they are processed or stored, as well as for tobacco and many kinds of nursery stock.

Methyl bromide is a gas at ordinary temperature; boiling at ~ 5 °C and solidifying at -93 °C; it has a density of 1.732 at 0 °C. The low boiling point of methyl bromide makes it possible to recover the product conveniently, even on a relatively large scale, by using the refrigeration. Some manufacturers however prefer compression liquefaction for its recovery especially for very large production rates<sup>(2)</sup>.

Commercial and laboratory methods of manufacturing methyl bromide are generally similar and are based primarily upon the reaction of hydrobromic acid with methanol. For the generation of the acid in contact with alcohol, the best known process is its liberation from the alkali bromide with sulfuric acid. Other methods involve the direct use of hydrobromic acid or the treatment of bromine with a reducing agent, such as sulfur dioxide or phosphorous, in the presence of water<sup>(3)</sup>.

The determination of the reaction rate expression involves two steps procedure. First, the concentration dependence is determined at a fixed temperature. Second, the temperature dependence of the reaction rate constant is evaluated by Arrhenius equation to give a complete reaction rate expression.

The problem reduces to that of determining the form of the concentration dependence and the value of the rate constant at the temperature of the experiment<sup>(4)</sup>.

Differential and integral methods are based on differentiation of experimental concentration versus

time data in order to obtain the actual rate of reaction. In these approaches one analyzes the data by postulating various functional relations between the rate of reaction and the concentrations of the various species in the reaction mixture and tests these hypotheses using appropriate plots<sup>(5)</sup>.

The common kinetic equation used for the reaction order estimation is:

$$\text{Log } r = \text{log } k' + m \text{ log } C_A \dots(1)$$

The constant  $k'$  and  $m$  may be determined from a log-log plot of the rate versus  $C_A$ . This procedure leads to a value of the overall order of the reaction<sup>(4)</sup>.

Another differential method useful in the determination of reaction rate expressions is the initial rate approach. It involves a series of rate measurements at different initial reactant concentrations but restricted to very small conversion of limiting reagent (5 to 10% or less). This technique differs from those mentioned previously in that lower conversions are used and each rate measurement involves a new experiment.

In an initial rate study, one focuses on the conditions that prevail at the start of the reaction. Since the concentrations of the various species do not undergo large changes during this period (varying by 10% at the most), one may characterize these concentrations by initial or average values that can then be substituted directly into the trial rate expression. One may determine the values of the reaction rate corresponding to zero time by measuring the initial slopes of concentration values versus time curves in constant volume system<sup>(4)</sup>.

The integral method of analysis always puts a specific rate equation to the test by integrating and comparing the predicted  $C$  versus  $t$  curve with experimental  $C$  versus  $t$  data.

## EXPERIMENTAL ARRANGEMENT AND PROCEDURE

## 1. Raw Materials

## 1.1 Hydrobromic acid

Technical (AJAX chemicals) 47 to 49 % w/w hydrobromic acid is used (density, 1.48 g/ml, at 20 °C; boiling point, 126 °C; and freezing point -11 °C). It is clear, colorless to pale yellow liquid when freshly prepared, becoming yellow to brown due to liberation of bromine.

## 1.2 Methanol

Methanol (Hopkin and Williams) of 99.5 % purity is used (density, 0.97 g/ml at 20 °C; boiling point, 64.7 °C; and freezing point -98 °C).

## 1.3 Catalyst

Sulfuric acid (BDH limited poole England) of 98 % purity is used as a catalyst (density, 1.84 g/ml at 20 °C; freezing point 10.5 °C; and decomposes at 340 °C).

## 2. Experimental Procedure.

Methanol is placed into the glass reactor, 2, Fig(1) and the heater is switched on to achieve a temperature of about 30 °C, then hydrobromic acid is added by means of separating funnel, 5, at a rate of about 28 cc./min. This addition will raise the temperature to about 40 °C. After that sulfuric acid is added slowly

at a rate about 5 cc./min. to the reaction mixture. This addition will raise the temperature to about 55 °C.

Then the reaction mixture is heated to the desired reaction temperature with continuous stirring. This temperature is kept constant during the desired duration time by means of a stirrer hot plate. The product is distilled out through a water reflux condenser, 3, at 25-30 °C. The main part of unreacted materials (methanol, hydrobromic acid, and sulfuric acid) is returned to the reaction vessel. Then methyl bromide gas with small quantity of unreacted material are passed through the absorber, 6, where water dissolves all unreacted materials, knowing that methyl bromide is very slightly soluble in water.

Subsequently methyl bromide gas is passed through silica gel column, 7, to remove all traces of moisture. The dry methyl bromide gas enters the two condensers, 8, 9, where it is condensed at (-10 to -15 °C).

The condensed methyl bromide is collected in a flask receiver, 9, which is submerged in a cooled ethanol bath, 10, at (-5 to -8 °C). The collected methyl bromide liquid is stored in a tight glass container which is kept in the cooling bath.

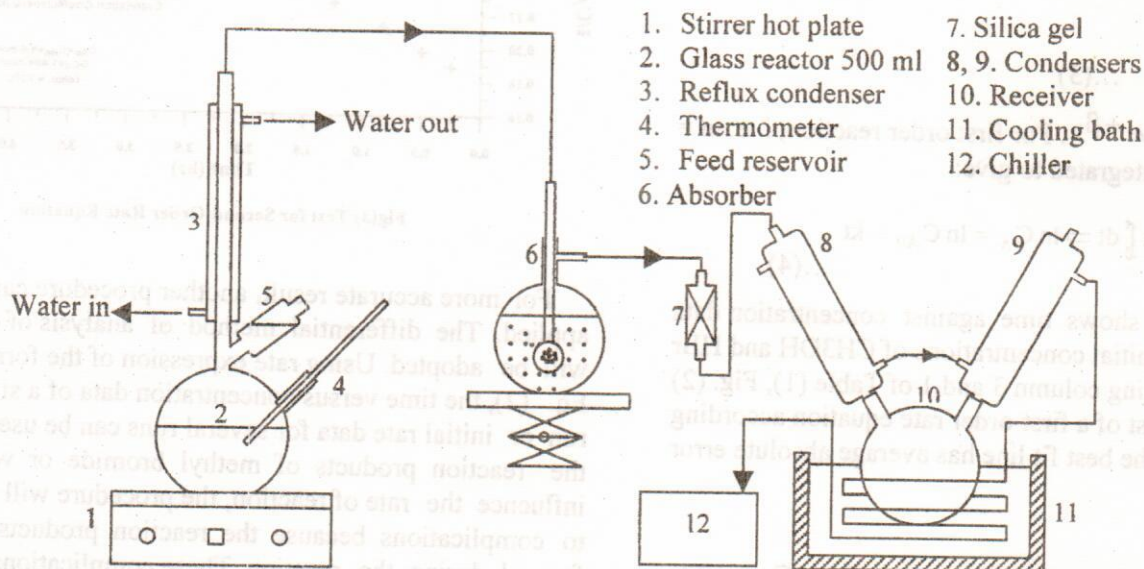


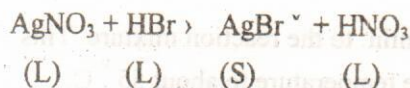
Fig.(1) Experimental Unit

## 3. Chemical Analysis.

## 3.1 Determination of an unreacted hydrobromic acid

Volhard's method is adopted to determine the bromide ions for the unreacted hydrobromic acid.

This method states that the bromide solution is acidified with dilute nitric acid. An excess of standard 0.1 N silver nitrate is added, the mixture thoroughly shaken to precipitate the bromide ions as silver bromide<sup>(28,29)</sup> according to the following reaction:



The residual silver nitrate is determined by means of titration with standard 0.1 N ammonium thiocyanate, using ferric alum as an indicator. A 1 ml of the thiocyanate should be equivalent to 1 ml of silver nitrate solution. The formation of orange-pink ferric thiocyanate indicates the complete reaction.

1 ml of 0.1 N AgNO<sub>3</sub> = 0.007992 g Br = 0.008093 g HBr

Then the percentage of HBr or bromine content can be determined.

## RESULTS AND DISCUSSION

### 1. Search for Rate Equation by Integral Analysis

The overall order of reaction can be tested for both first and second-order by using equal initial concentrations of methanol and hydrobromic acid. Since the reaction is bimolecular, the rate expression can be written in the form of

$$r = kC_A^{\beta_A} C_B^{\beta_B} \quad \dots(2)$$

where A and B refer to hydrobromic acid and methanol respectively.

Since,  $C_{A_0} = C_{B_0}$ , Equation (2) can be written in the form of:

$$-r_A = kC_A^m \quad \dots(3)$$

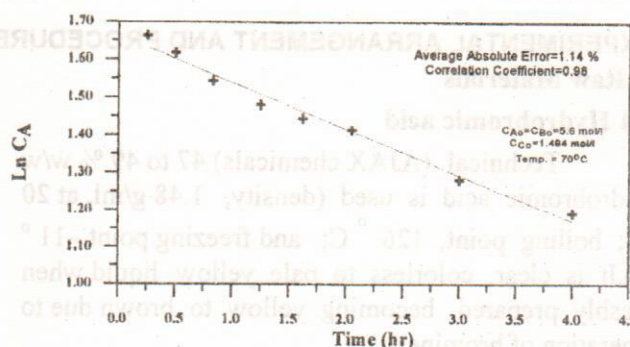
where  $m = \beta_A + \beta_B$ . For first order reaction, i. e.  $m = 1$ , Eq. (3) is integrated to give:

$$-\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt \Rightarrow \ln C_A = \ln C_{A_0} - kt \quad \dots(4)$$

Table (1) shows time against concentration data using equal initial concentrations of CH<sub>3</sub>OH and HBr at 70 °C. Using column 3 and 1 of Table (1), Fig. (2) shows the test of a first-order rate equation according to Eq.(4). The best fit line has average absolute error of 1.14%.

Table (1) C<sub>A</sub> versus Time Data Using C<sub>A0</sub> = C<sub>B0</sub> = 5.62 and C<sub>C0</sub> = 1.494 mol/l at 70 °C

C <sub>A</sub> (mol/l)	Time (hr)	Ln C <sub>A</sub>	1/C <sub>A</sub>
5.28	0.25	1.664	0.189
5.04	0.50	1.617	0.198
4.69	0.83	1.545	0.213
4.4	1.25	1.482	0.227
4.24	1.62	1.445	0.236
4.12	2.05	1.416	0.243
3.16	3.00	1.284	0.277
3.3	4.00	1.194	0.303

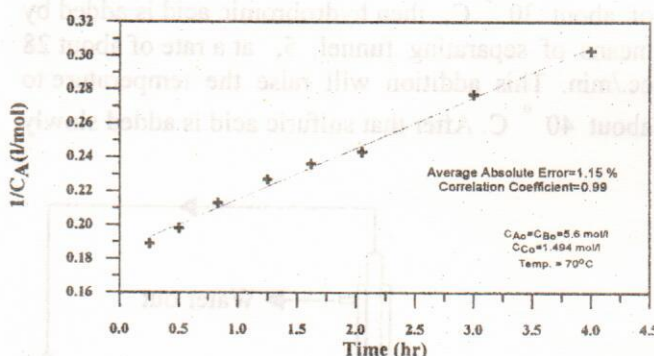


Fig(2) Test for First-Order Rate Equation

For second-order reaction, i. e.  $m = 2$ , Eq. (3) is integrated to give:

$$-\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A^2} = k \int_0^t dt \Rightarrow \frac{1}{C_A} = \frac{1}{C_{A_0}} + kt \quad \dots(5)$$

Using column 1 and 4 of Table (1), Fig. (3) shows the test for second order rate equation according to Eq. (5). The best fit line has an average absolute error of 1.15%. However the two tests of first and second-order don't give a distinct difference between them since they nearly makes a straight lines.



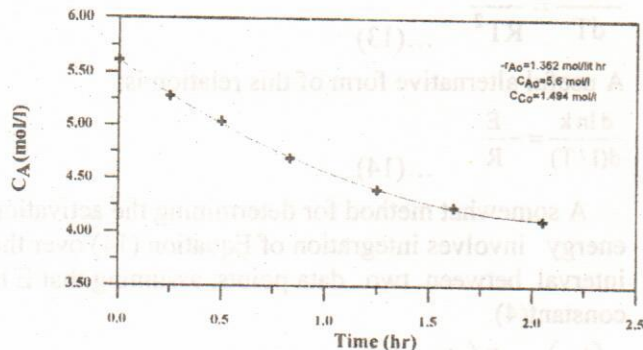
Fig(3) Test for Second-Order Rate Equation

For more accurate result, another procedure can be applied. The differential method of analysis of data will be adopted. Using rate expression of the form of Eq. (2), the time versus concentration data of a single run or initial rate data for several runs can be used. If the reaction products of methyl bromide or water influence the rate of reaction, the procedure will lead to complications because the reaction products are formed during the reaction. These complications are avoided if the initial rate data are analyzed which it has less chance of getting in trouble.

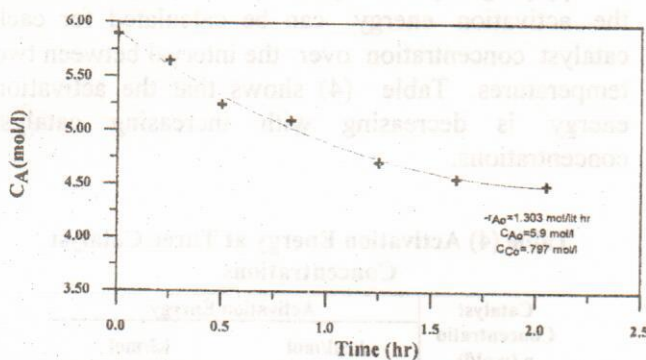
### 2. Initial Rate Measurements

The data consist of three time-concentration runs which use equal initial concentrations of methanol and hydrobromic acid at 70 °C. Each run uses a new initial concentration. The data of one of the three runs are shown in Table (1).

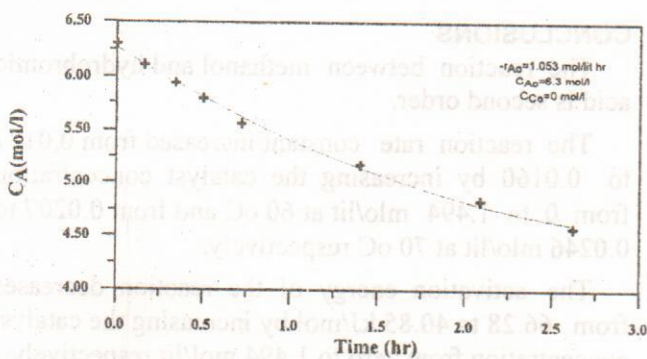
Initial rates of reaction are found by plotting the concentration versus time and finding the slopes at  $t = 0$  as shown in Figures (4), (5), and (6) for the runs of the three experiments. Table (2) shows the initial rate measurements at three different initial concentrations and 70 oC.



Fig(4) Hydrobromic Acid Concentration vs. Time Using Initial Concentration of 5.6 mol/l and 70°C



Fig(5) Hydrobromic Acid Concentration vs. Time Using Initial Concentration of 5.9 mol/l and 70°C



Fig(6) Hydrobromic Acid Concentration vs. Time Using Initial Concentration of 6.3 mol/l and 70°C

Taking the logarithm for Eq. (3):

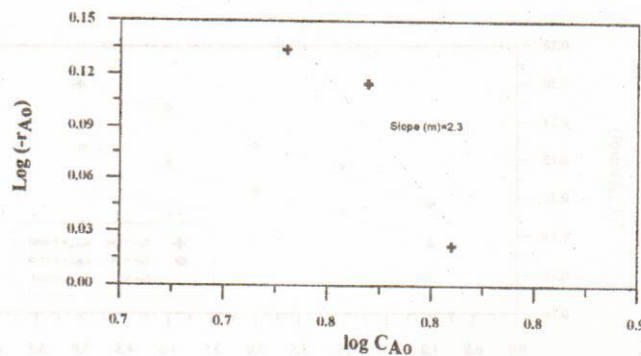
$$\log(-r_A) = \log k + m \log C_A \quad \dots(6)$$

Using the data of Table (2), the overall order of reaction can be found by plotting  $\log(-r_A)$  versus  $\log C_A$  as shown in Fig. (7). The slope (m) is found to be (2.3). So the reaction is considered as second-order which agree with the literature (8).

The reactants concentrations are increased at the expense of decreasing the catalyst concentration. This leads to decreasing the rate of reaction with increasing the reactants concentrations.

Table (2) Initial Rate Measurement at three Initial Concentrations and 70 °C

Run No.	$C_{A0}=C_{B0}$ (mol/l)	$C_C$ (mol/l)	$-r_{A0}$ (mol/l hr)	$\text{Log } C_{A0}$	$\text{Log } (-r_{A0})$
1	5.6	1.494	1.362	0.748	0.134
2	5.9	0.797	1.303	0.772	0.1149
3	6.3	0	1.053	0.796	0.022



Fig(7) Log ( $r_{A0}$ ) vs.  $\log C_{A0}$  Using Initial Rate Data

### 3. Catalyst Concentration Dependence of Reaction Rate Constant

The experimental results have shown that the reaction of CH<sub>3</sub>OH and HBr can proceed even without catalyst, the overall rate of reaction can be considered as the sum of the rates of both uncatalyzed and catalyzed reactions(5). Using equal concentrations of methanol and hydrobromic acid, the reaction rate expression of Equation (3) for  $m = 2$  can be written in the following form:

$$-\frac{dC_A}{dt} = (k_1 + k_2 C_c) C_A^2 \quad \dots(7)$$

where  $k_1$  and  $k_2$  represent the reaction rate constants of uncatalyzed and catalyzed reactions. The observed reaction rate constant can be considered as follows:

$$k_{obs} = k_1 + k_2 C_c$$

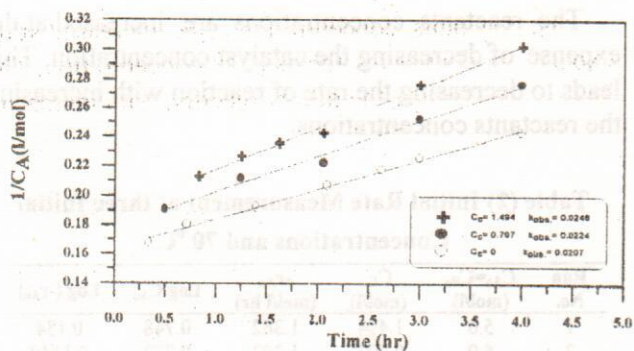
Integrating Equation (7) gives:

$$\frac{1}{C_A} = \frac{1}{C_{A_0}} + (k_1 + k_2 C_c) t \quad \dots(8)$$

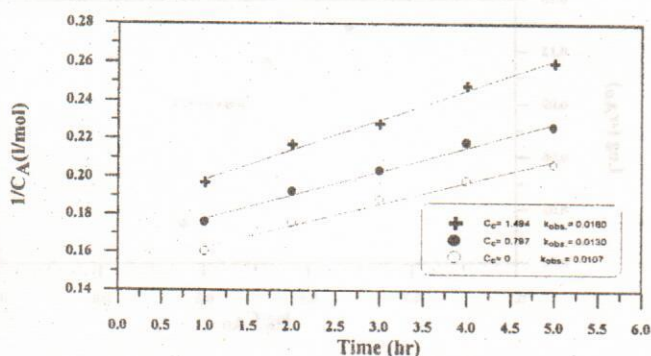
$$\text{OR} \quad \frac{1}{C_A} = \frac{1}{C_{A_0}} + k_{obs} t \quad \dots(9)$$

Several values of  $k_{obs}$  can be calculated at certain temperatures by making a series of runs at various catalyst concentrations. These runs allow to find  $k_1$  and  $k_2$ .

Figure (8) shows the plot of  $1/C_A$  versus time of three runs at three catalyst concentrations of 0, 0.779, and 1.494 mol/lit at 60 oC. Fig. (9) shows the plot of another three runs at the same catalyst concentrations and 70 oC.



Fig(8) 1/CA vs. Time at Different Catalyst Concentrations and 70 °C



Fig(9) 1/CA vs. Time at Different Catalyst Concentrations and 60 °C

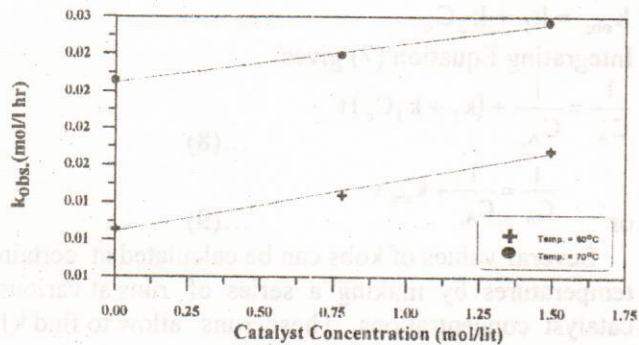
Table (3) represents the calculated values of kobs. Plotting kobs versus Cc, k1, and k2 can be calculated at each temperature Fig. (10).

$$k_{obs} = 0.0106 + 0.354C_c \quad \text{at } T = 60 \text{ oC} \dots (10)$$

$$k_{obs} = 0.0206 + 0.260C_c \quad \text{at } T = 70 \text{ oC} \dots (11)$$

Table (3) kobs. Values at Three Catalyst Concentrations and Two Temperatures

Temp. (°C)	Catalyst Concentration (mol/l)		
	0	0.779	1.494
60	0.0107	0.0130	0.0160
70	0.0207	0.0224	0.0246



Fig(10) kobs vs. Catalyst Concentration at 60 and 70 °C

#### 4. Determination of Activation Energy

Arrhenius equation gives the effect of temperature on the rate constant.

$$k = A \exp\left(-\frac{E}{RT}\right) \dots (12)$$

The variation of k with temperature may be determined by differentiating the logarithmic form of the equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \dots (13)$$

A useful alternative form of this relation is:

$$\frac{d \ln k}{d(1/T)} = -\frac{E}{R} \dots (14)$$

A somewhat method for determining the activation energy involves integration of Equation (14) over the interval between two data points, assuming that E is constant(4).

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \dots (15)$$

Applying Equation (15) for the data of table (3), the activation energy can be calculated for each catalyst concentration over the interval between two temperatures. Table (4) shows that the activation energy is decreasing with increasing catalyst concentrations.

Table (4) Activation Energy at Three Catalyst Concentrations

Catalyst Concentration n (mol/l)	Activation Energy	
	kcal/mol	kJ/mol
0	15.78	66.28
0.779	12.31	51.67
1.494	9.73	40.85

#### CONCLUSIONS

The reaction between methanol and hydrobromic acid is second order.

The reaction rate constant increased from 0,0107 to 0.0160 by increasing the catalyst concentration from 0 to 1.494 mlo/lit at 60 oC and from 0.0207 to 0.0246 mlo/lit at 70 oC respectively.

The activation energy of the reaction decreases from 66.28 to 40.85 kJ/mol by increasing the catalyst concentration from zero to 1.494 mol/lit respectively.

#### NOMENCLATURE

C	Concentration	mol/lit
E	Activation energy	kJ/mol
K	Reaction rate constant	(mol/lit) <sup>-1</sup> mh <sup>-1</sup>
m	Overall order of reaction	
R	Gas constant	
R	Reaction rate	mol/lit h
T	Temperature	oC
t	Time	h

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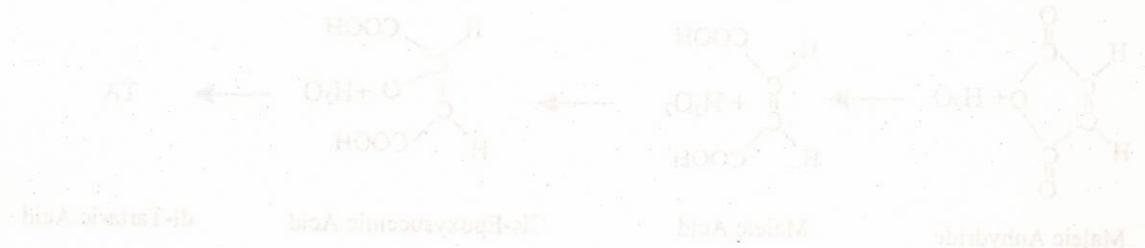
as its acid potassium salt (cream of tartar) potassium bitartrate, potassium bitartrate, KHC<sub>4</sub>O<sub>6</sub>. In the fermentation of grape juice to wine the tartrate deposits in the fermentation vessels. The tartrate crystallized tartaric acid was first obtained from such fermentation residues by Scheele in 1789 and even today this continues to be the chief source of industrial acid.

L-(+)-tartaric acid is produced commercially by conversion of the crude cream of tartar to calcium tartrate which is decomposed with dilute sulfuric acid to tartaric acid and calcium sulfate.

In Europe, South Africa and Japan racemic (R,R)-tartaric acid (the tartaric acid) is also produced commercially. It is obtained synthetically by treatment of maleic acid or its anhydride with hydrogen peroxide in the presence of a catalyst of tungstic acid.<sup>10</sup>

The present work is concerned with preparation of synthetic di-tartaric (racemic) acid by hydrolysis of maleic anhydride. The major aim in this production is the two raw materials, hydrogen peroxide and maleic anhydride. Hydrogen peroxide has had a history of good stability on process and availability. Maleic anhydride can be prepared in large quantities by oxidation of n-butane, the basic and detailed design of this project is available in the literature of industry.

The chemical reaction for the production of di-tartaric acid is represented by:



INTRODUCTION

Tartaric acid and 2,3-dihydroxybutanedioic acid are dicarboxylic acids, C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>, containing two hydroxyl and two carboxyl groups attached to an ethane hydrocarbon structure. Tartaric acid exists as a racemate.

Tartaric acid is used in the production of food and drugs. It exists in four modifications namely dextro-tartaric acid and levo-tartaric acid which exhibit optical activity, and meso- (dl-tartaric) acid and meso-tartaric acid which are optically inactive.<sup>11</sup>

Dextro-tartaric acid and levo-tartaric acid have the same physical properties except for their rotation of plane-polarized light, specific rotation  $[\alpha]_D^{25}$  and bearing the mirror-image relationship to each other.

Racemic acid is a molecular compound, all its crystal contain equal number of molecules of the d and l isomers. It is optically inactive and can be separated into the active forms.

Meso-tartaric acid has no effect upon the plane of polarization of plane-polarized light. It is optically inactive and can not be separated into the two active forms.

The main commercial product in the world is the natural, dextro-tartaric form (R,R)-tartaric acid, L-(+)-tartaric acid. This enantiomer occurs in grapes