

A CASE STUDY FOR THE MANUFACTURE OF SODIUM
HYDROGEN CARBONATE

By

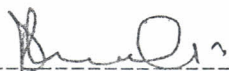
DAVID KINUTHIA KARIUKI

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other University.

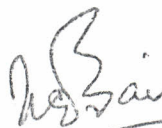


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(i)

Dedicated to my mother MRS. HELEN W. KARIUKI

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ABSTRACT

Sodium hydrogen carbonate is used extensively in the baking and pharmaceutical industries, where it is required in very high purity. Commercially, it is prepared through the solvay process.

In this project methods of preparing high purity grade sodium hydrogen carbonate from Magadi soda have been investigated. The method studied involves the carbonation of soda ash at varying temperatures, pressures and stirring times.

Determinations of sodium carbonate and sodium hydrogen carbonate concentrations were carried out titrimetrically using methyl orange-indigo carmine and thymol blue-cresol red mixed indicators at pH 3.8 and pH 8.3 respectively. This method gave an accuracy of $97\% \pm 1.9\%$ for concentrations upto 10 ppm.

Factors affecting the separation of sodium hydrogen carbonate from the sodium carbonate solution have also been studied. The solubilities of the two salts differ greatly at 40°C and this has been shown to be the best temperature at which pure crystals of sodium hydrogen carbonate are formed. It has also been shown, through mutual solubility studies, that solubility of sodium hydrogen carbonate in saturated sodium carbonate solution is very low, 0.23g NaHCO_3 in $51\text{g Na}_2\text{CO}_3/100\text{g H}_2\text{O}$.

The optimum conditions for the manufacture of sodium hydrogen carbonate have therefore been shown to be 40°C , 2.5 kg/cm^2 pressure and stirring time of 3 hours. Under these

(iv)

conditions the yield obtained was $41\% \pm 1.1\%$ sodium hydrogen carbonate with a purity of $90\% \pm 1.6\%$. The main impurity being water at about 10%.

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CHAPTER ONE

1.1 INTRODUCTION

Sodium hydrogen carbonate, also known as sodium bicarbonate is an article of commerce and is commonly referred to as baking soda.

It is rarely found, as a mineral in natural deposits, and hence most of it is processed [1].

However, pure sodium hydrogen carbonate crystals have been detected at the bed of Lake Magadi in Kenya's Rift Valley, amongst crystals of trona, but in low quantity [2].

Sodium hydrogen carbonate is largely used in the baking industry, as an ingredient in the manufacture of baking powder. It is also used in the pharmaceuticals as an anti-acid and in drugs and general medicines. In food industries, particularly drinks, it is used as a preservative or a source of carbon dioxide [3]. All these uses require sodium hydrogen carbonate of very high purity. In low purity, sodium hydrogen carbonate is used as a fire extinguisher and also in laundry as a mild detergent [4].

All sodium hydrogen carbonate requirement for this country is met by foreign imports.

Import statistics for sodium hydrogen carbonate for the last seven years are summarised below in Table 1:1.

TABLE 1:1 * IMPORTS AND PRICES OF SODIUM HYDROGEN CARBONATE 1980-1986

YEAR	QUANTITY (tons)	VALUE (KSh. millions)
1980	15,000	195
1981	14,900	207
1982	15,100	224
1983	16,000	231
1984	17,500	270
1985	17,900	290
1986	18,100	300
TOTAL	114,500	1717
AVERAGE	16,360	245

It is evident from the table that the use of sodium hydrogen carbonate in this country is increasing with years. This can be attributed to population growth. Kenya has a population increase rate of 3.4% per annum and since sodium hydrogen carbonate is a consumer product, it will have a direct proportion relationship [5]. Likewise there is an increase of foreign exchange loss as the demand for sodium hydrogen carbonate increases.

In a bulletin of minerals of Kenya (1970) by Dubois and revised by Walsh, it is reported that Magadi Soda Co. Ltd. produced bicarbonate of soda (sodium hydrogen carbonate) in the 1950s mainly as a source of carbon dioxide gas for the local

mineral-water manufacturers [6]. This was later abandoned and methods of production were not stated. It is not possible to say whether the company extracted, mined or processed their sodium hydrogen carbonate.

Later in the years, pure carbon dioxide was discovered and mined for local manufacturers as stated in the later sections of this thesis [6].

The sodium hydrogen carbonate content in trona, the mineral found in Lake Magadi, is small in quantity for any economical mining. This explains why the trona is referred to as natural soda, other salts are in trace amounts [2].

Sodium hydrogen carbonate can be manufactured from its normal carbonate by the action of carbon dioxide and water [4]. It is also produced from sodium chloride, and trona as explained in the later sections of this work. All of these raw materials are locally available.

Sodium hydrogen carbonate crystallises out from its aqueous solutions as its solubility is quite low compared to that of sodium carbonate, sodium chloride or sodium sulphate among other impurities or raw materials used for its production [9].

The difficulty of obtaining pure sodium hydrogen carbonate is overcome if start is made with purified raw materials. In this connection, one thinks of the possibility of obtaining sodium hydrogen carbonate from pure sodium carbonate and carbon dioxide.

A look at these two raw materials and their availability is given in the following few paragraphs.

1.1.1 SODIUM CARBONATE

Sodium carbonate of high purity can be obtained from Magadi Soda Company Kenya Ltd. That is soda ash which is the main product followed by sodium chloride (table salt) [24].

Magadi soda ash is Kenya's most important mineral resource. It is mined from trona (sodium sesquicarbonate- $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). The deposits of trona are estimated to be over 200 million tons of which 40 million tons are in the upper layer [2]. They are inexhaustible since there is a continuous addition by the action of certain fungi and algae on sodium sulphate reducing it to sodium sulphide. Carbon dioxide in the soil and atmosphere then converts sodium sulphide into sodium carbonate with evolution of hydrogen sulphide [2]. This could be the reason behind the many sources of hydrogen sulphide along the Rift Valley and in particular near lake Magadi, e.g. Hells Gate and lake Bogoria and the obvious strong hydrogen sulphide smell at lake Magadi.

The cycle for the water, from streams, reaching the lake after the rains, is estimated to be sixteen years [2,6].

1.1.2 MINING OPERATIONS OF SODIUM CARBONATE

The raw material (trona) is dug by a dredge which floats in a shallow paddock. The lake liquor level is not far below the trona surface and the dredge remains more or less at ground-level and is designed to cut to at least eight feet below trona surface. From the dredge buckets, raw trona is passed down a chute to the first breakers which crush it to fragments not exceeding six inches in size, while the second breakers crush it to two inch size.

From the breakers the trona goes under an electromagnetic separator to separate impurities of iron as it passes to a vibrating screen. It is then mixed with lake liquor from the lake, pumped in by an eight-inch centrifugal self-priming pump. The slurry is pumped through a pipeline to the factory at an approximately 3600 litres per minute. Along the pipeline are booster stations, to maintain the pressure [6].

On arrival at the ash plant, the slurry is passed into dewatering trommel where the oversize material is crushed in the second trommel. It is washed with relatively dilute liquor from the 'fish springs' east of the factory. The fine material from the first trommel and also from the second trommel is carried as a slurry to four settling cores arranged in parallel, the overflow going to waste in the lake, and the settled fine material from the settling cones are fed into a stirring tank and into two centrifuges [6].

The whole idea boils down to centrifuge. The liquor drained off goes to waste while the "trona crystal mush" is carried by screw conveyor to the soda stock floor where excess liquor is allowed to drain off. This is termed as the wet side.

In the dry side, the stocked trona is shovelled on to portable conveyor belts which feed an elevator followed by a screw conveyor which supply the cylinders with hot gases at about 1200°C from the furnace at one end, passing through them.

Trona is introduced from the opposite end and the heat from the gases converts the crystals of trona (sodium sesquicarbonate) into soda ash (sodium carbonate). The average throughput of ash is in the region of 250 to 290 tons per day.

The calciners are worked continuously on a shift basis. The soda ash leaving the calciners is fed to pulverizing mills and to screens for size, from where it is put into silo for storage.

It is then weighed into required amount in woven polypropylene sacks with a polythene liner [2,6]. (See diagram 1:1).

A chemical analysis of the soda ash reported by Magadi chemical laboratory is given below:-

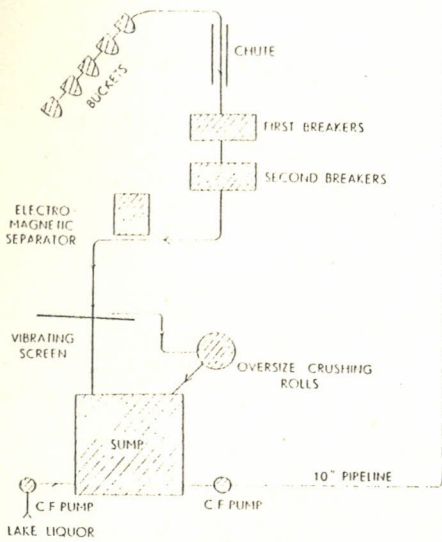
	%
Soda alkalinity (Na_2CO_3)	97.33
Sodium fluoride (NaF)	0.9
Sodium chloride (NaCl)	0.45
Sodium sulphate (Na_2SO_4)	0.48
Sodium bicarbonate (NaHCO_3)	0.25
Iron oxide (Fe_2O_3)	0.02
Other water insoluble	0.33

[6]

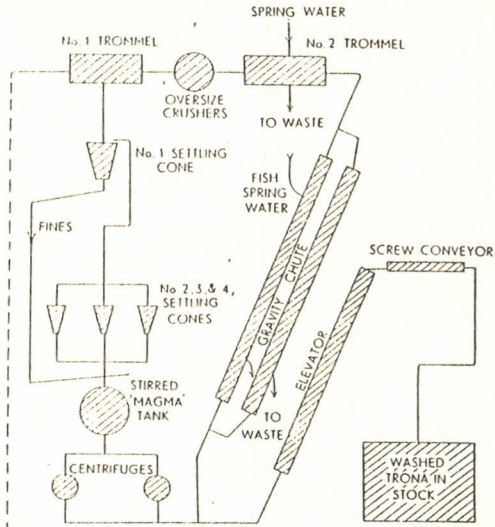
The factory has an installed capacity of 250,000 tons per year, but it rarely approaches this capacity due to marketing and transport (to the port) problems. The factory produces about 100,000 tons per year on average. Most of Magadi soda ash is exported [7]. The export statistics for the last seven years are summarised below in Table 1:2.

DIAGRAM 1:1 MAGADI DREDGE AND ASH PLANT

DREDGE



ASH PLANT-'WET SIDE'



ASH PLANT-'DRY SIDE'

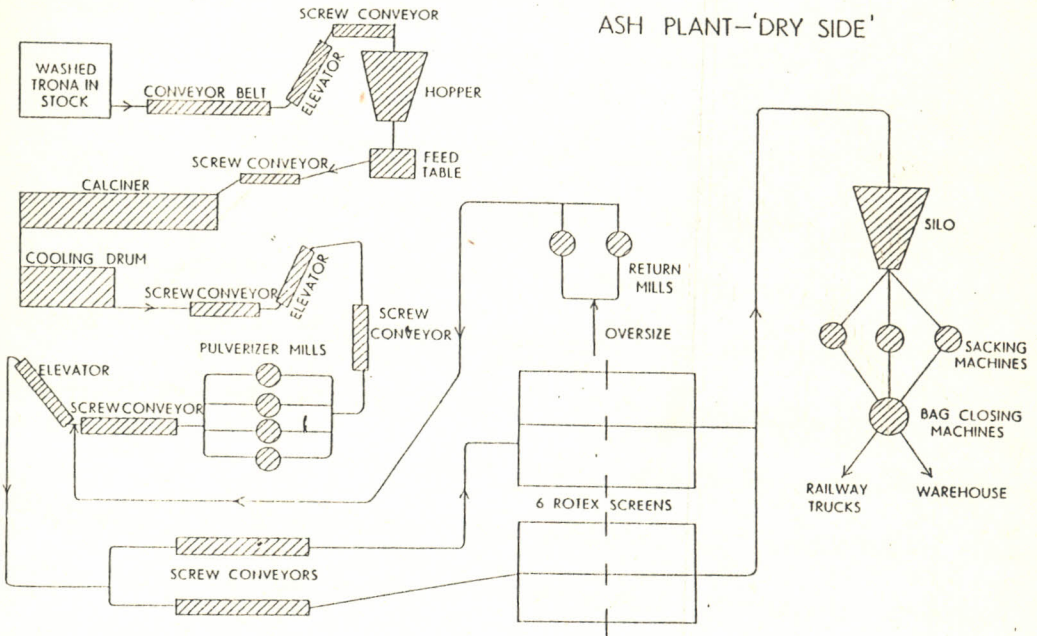


TABLE 1:2 • SODA ASH EXPORTS AND PRICES 1980-1986

YEAR	QUANTITY (tons)	VALUE (KSh. million)
1980	160,300	505
1981	200,080	630
1982	143,480	452
1983	139,600	440
1984	191,400	603
1985	170,530	537
1986	121,040	381
TOTAL	1,126,430	3,548
AVERAGE	160,918	507

Magadi soda ash, despite long distances to the Mombasa port is still competitive (price wise) in the export market. The main consumers of the ash, are the Indian Ocean Islands, Australia, Israel, South American countries and the Far East, all of them accounting for over 70% of the total sales.

The soda ash consumers, mostly use it for glass industries, followed by soap and other detergents making, and also in chemical industry where they convert it to refined bicarbonate, caustic soda, sodium silicate, drugs, dyestuffs and chemicals for the cotton, rayon and paper industries etc.

It also finds a large use in water softening, refining oils and in **desulphurizing** steel which is a metallurgical process [6,7,4].

The export statistics show that inspite of the much talked about sodium fluoride impurity in Magadi soda, it still finds much use in commodities requiring high purity.

Locally, Magadi soda is rarely used. Much of it is used in the slowly growing glass industry and in the water treatment. Both of these do not use even a tenth of the factory production.

The Kenya Government all the same do import sodium carbonate for its other uses. This is believed to be of higher purity and quality and hence suitable for other uses other than the two mentioned above. It is imported in various forms namely anhydrous sodium carbonate, sodium carbonate monohydrate, sodium carbonate decahydrate etc.

Import statistics of various forms of sodium carbonate for the last seven years are summarised below in Table 1:3.

TABLE 1:3 IMPORTS AND PRICES OF SODIUM CARBONATE
1980-1986

YEAR	QUANTITY (tons)	VALUE (KSh millions)
1980	17,000	190.5
1981	18,000	202
1982	19,000	211
1983	20,000	224
1984	21,000	225
1985	22,500	250
1986	24,000	270
TOTAL	141,500	1,572.5
AVERAGE	20,215	224.6

It is clear from the above Table 1:3 that much foreign exchange is used for the importation of a commodity that is locally available. Moreover, with the increasing population more and more sodium carbonate is bound to be imported hence loss of foreign exchange that this nation needs.

Other alkali demand like caustic soda will also be on the increase as the population soars. At present the production of caustic soda worldwide is being curtailed. Caustic soda is mainly produced by the electrolysis of brine. This also produces hydrochloric acid or rather chlorine which contributes to the chlorinated fluoro carbons which are believed to be responsible for the depletion of the ozone layer, the creation of the hole through the ozone layer [2,6].

Where the substitution of caustic soda by soda ash is possible, soda ash is replacing caustic soda as the latter is becoming scarce and hence more expensive. In this case demand of soda ash, and that of Magadi soda in particular will increase as the caustic soda becomes uneconomical to use.

The Kenya Government is urged to use this opportunity in using and marketing sodium carbonate wherever possible so as to benefit from the increase in sales of Magadi soda. This will earn the Government more foreign exchange and also create employment.

1.1.3 CARBON DIOXIDE

Carbon dioxide occurs naturally though it can as well be produced from carbonates reacting with acids. It is known to occur in holes and fissures in volcanic rocks.

Carbon dioxide gas was first discovered in 1918 in Kedong valley where it was tapped for small commercial use. In 1922, seepages of the gas were discovered in the soil and rocks south of Lake Magadi but were not tapped for any use [6].

It was in 1946 that a borehole sunk at Esageri near Eldama Ravine struck the gas at a depth of 450 ft and at a pressure of 80 psi, averaging 98% carbon dioxide. Real commercial exploitation was then begun. This did not continue for a long period due to the caving in of the borehole.

Present day demand for carbon dioxide is met by a mine at Kerita near Uplands, some 40 kilometers north-west of Nairobi. This borehole was sunk in 1957 and encountered gas at a pressure of about 35 psi. A commercial analysis of the gas done by Carbacid Company Ltd. gave the following composition.

Carbon dioxide	97.8%
Oxygen	0.2%
Hydrocarbons as methane	1.1%
Argon and other inert gases	0.07%
Nitrogen (by difference)	<u>0.8%</u>
Total	99.99%

The gas is mined by Carbacid Co. Ltd. a local company which bought the shares from Kagwe Ltd. The gas is sold compressed in steel cylinders and also in solid form as 'dry ice'.

'Dry ice' is locally used mainly as a refrigerant in the storage and transportation of perishable foodstuff e.g. meat, vegetables and fish as it also inhibits growth of bacteria and

moulds while liquid gas is used for aerated drinks.

The gas as it comes to the surface could also be used as a prime-mover to generate some electric power. The combined production of commercially exploited sources of natural carbon dioxide gas is given below in Table 1:4.

TABLE 1:4 PRODUCTION OF CARBON DIOXIDE GAS 1980-1986

YEAR	QUANTITY (long tons)	VALUE (KSh.millions)
1980	1500	12.75
1981	1610	13.70
1982	1660	14.00
1983	1750	15.00
1984	1800	15.50
1985	1900	16.00
1986	1970	17.00
TOTAL	12,190	104.00
AVERAGE	1,741	15.0

[4,6,7,8]

From the table 1:4 above it can be deduced that carbon dioxide also plays an important role in the economy of our country. An increased demand would be effected if more economical use of the gas could be found.

1.1.4 WATER

Water is plenty in Kenya. There is enough rains to supply any large industry that would require plenty of water.

Although carbonation of sodium carbonate involves only old-traditional chemistry, very little work has been reported. In particular, in this country apart from the analysis of Magadi soda, that has thoroughly been investigated, other related work on Magadi soda has not been done. More research on exhaustive utilization of the soda need to be done.

Therefore a successful investigation into the production of sodium hydrogen carbonate from sodium carbonate, carbon dioxide and water as raw materials would be of great economical use of the country. This would earn and save foreign exchange which is an important aim in any country and would also create employment.

CHAPTER TWO

2.1 LITERATURE SURVEY

It has been pointed out in the introduction that sodium hydrogen carbonate can be prepared by various methods. In the following paragraphs, a review of the literature dealing with the different methods is given.

Work on the preparation of sodium hydrogen carbonate has been carried out for some time. Narwani and Dharmaney of India in 1942 [9] electrolysed a clear solution of natural soda. The natural soda contained 20% of sodium carbonate, sodium sulphate and sodium chloride. The electrolysis was carried out at an average current density of 4-5 amperes per square decimeter in a McDonald cell. The diaphragm used was of thick asbestos paper treated with a saturated solution of sodium silicate.

The cathode compartment yielded sodium carbonate with low sodium sulphate impurity after crystallization. This was because of the excess carbonate and sulphate ions in the solution and the low solubility differences of sodium carbonate and sodium sulphate. Otherwise the first ionisation of sodium carbonate should have given sodium hydroxide at the cathode. At the anode compartment, pure sodium hydrogen carbonate was formed. The solubility of sodium hydrogen carbonate is quite low compared to that of the impurities present in the natural soda.



The sodium hydroxide combined with carbon dioxide in solution to form sodium carbonate at the cathode. The process, though of small production capacity, is important in the sense that, its raw material is impure natural soda that is processed to yield pure sodium hydrogen carbonate. Technical difficulties will of course be encountered particularly in maintaining sodium silicate solution at the diaphragm. Sodium silicate solution is bound to dissolve away into the natural soda solution. Very little is known of such electrodes that will separate natural soda in the above manner, hence more information and clearly designed methods are required in order to fully establish such a separation. This incapacitates the scaling up of such a separation though it is theoretically very impressive.

Angel [10] also separated sodium hydrogen carbonate from electrolytic soda dyes which had been saturated with salt and treated with excess carbon dioxide. The separation was done after electrolysis, by adding calcium chloride to the mother liquor. The introduction of calcium chloride brought difficulties in the purification of the final product ending up with low yields.

Later in 1971, Misumi [11] of Central Glass Company Ltd. of Japan described a process of preparing sodium hydrogen carbonate and hydrochloric acid through an electrolysis method. Electrolytic diaphragm for alkali was used. Carbon dioxide was passed through the electrolytic solution containing sodium hydroxide in the brine in the electrolytic cell. Sodium hydrogen carbonate separated out, and the mother liquor was recycled after it had been saturated with the crude sodium chloride. The yields were purified by adding calcium hydroxide. This was in the hope of precipitating magnesium hydroxide and calcium

carbonate. No harmful wastes were released and no large scale equipment such as evaporators and separators were required. This proved to be a high yielding low capital investment process. However little is said of the electrodes and the diaphragms or of the production of hydrochloric acid.

Alkali metal hydrogen carbonates can also be manufactured by the action of an alkali metal chloride, with carbon dioxide.

This was also investigated by Gol'd-shtein [12] of U.S.S.R in 1951 when he carbonated solutions of sodium chloride and ammonia at temperatures 30°, 40° and 60°C giving ammonium chloride and sodium hydrogen carbonate. The rate of crystallization of sodium hydrogen carbonate from supersaturated solution was found to be proportional to the cube of the degree of supersaturation. An increase in temperature and decrease in carbonation rate will decrease the degree of supersaturation. However, $\text{H}_2\text{NCO}_2\text{NH}_4$ was formed in the initial stages.

A similar method was discussed by Eliasoff [17] of Institute for Research and Development, Israel. He contacted brine containing 80 g/l of ammonia and 250 g/l sodium chloride at 220°C in four stages. This was done using kerosene which had been saturated with carbon dioxide at a pressure of five atmospheres at a contact time of ten minutes.

Sodium hydrogen carbonate was filtered from the aqueous phase which was then replenished with ammonia as the kerosene was returned for reloading with carbon dioxide. The yield for sodium hydrogen carbonate was high but of low purity due to the chloride and ammonia impurities involved in the processing.

Toyo soda company of Japan, as late as 1980, patented [14] a production method of sodium hydrogen carbonate. They suggested that sodium carbonate or sodium hydroxide of a given amount and carbon dioxide were fed to a reaction vessel at 40°C to 100°C. Sodium chloride was added and good crystals of sodium hydrogen carbonate were retrieved.

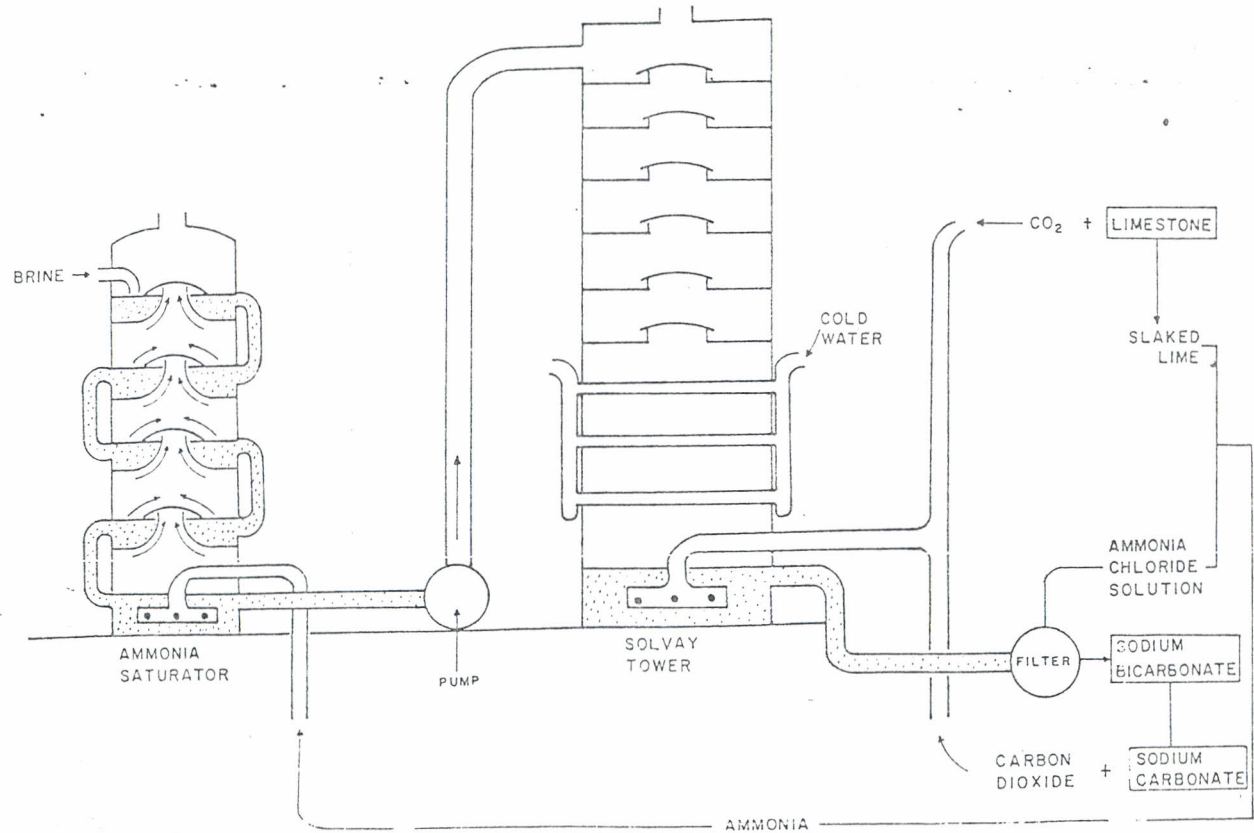
The most widely known commercial method for the production of sodium hydrogen carbonate is the solvay process. Solvay devised a method which is basically what has been described above. The process consists of brine saturated with both ammonia and carbon dioxide [15]. (See Figure 2:1).

The ammoniated brine was made by passing ammonia upwards the tall steel towers, against a stream of brine trickling downwards. The insoluble hydroxide settled out at the bottom and was filtered from the solution. In this absorption, heat is generated and since the optimum temperature for carbonation stage is 30°C, the ammoniated brine is then passed to the top of the solvay tower and trickles down against a stream of carbon dioxide at about two atmospheric pressure.

At the bottom of this tower, the materials are a white sludge of sodium hydrogen carbonate suspended in ammonium chloride solution. The mixture is separated by vacuum filtration.

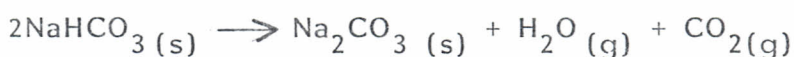
Vacuum filtration involves a large cylindrical drum with perforated sides covered by a suitable material which acts as the filter. The drum, the inside of which is divided into sections, rotates about its long axis and the lower part dips into a tank containing the sludge or magma. The pressure inside the lowest section of the drum is decreased so that ammonium chloride solution

FIGURE 2.1 : THE SOLVAY PROCESS



is sucked through the cloth, leaving the sodium hydrogen carbonate on the outside.

As the drum rotates, the solid is scrapped off by a long knife pressing against the filter. The precipitated sodium hydrogen carbonate contains sodium chloride, ammonium chloride and water as impurities. To obtain sodium carbonate, the impure sodium hydrogen carbonate is fed into calciners and heated by the flue gases. The sodium hydrogen carbonate decomposes to give sodium carbonate and the ammonium chloride sublimes off. The sodium carbonate formed has 1% sodium chloride impurity.



It is the intention of this work to show that sodium hydrogen carbonate can be obtained by the action of carbon dioxide on saturated sodium carbonate solution. That is to show the viability of the reverse of the above equation of processing sodium carbonate.



A survey of work directly related to this investigation is given below in the following few paragraphs.

Ebe [16] of Japan, in 1948 combined directly sodium carbonate and ammonium carbonate by grinding them together with some amount of water. The reaction product was spread on paper for drying. The ammonia sublimed out and the yield of sodium hydrogen carbonate was 70%. This unfortunately could only be done in minute amounts.

Sazonov [19] patented a carbonation process of sodium carbonate to produce sodium hydrogen carbonate. The sodium hydrogen carbonate was removed from the mother liquor, washed and dried. The rate of removal of sodium hydrogen carbonate suspension from the carbonation column regulated the carbonation. The suspension was a function of the amount of carbonic acid added with a correction for the temperature at the gas-liquid medium in the adsorption zone.

The Asahi Glass Company Ltd. of Japan [18] also patented a method of production of pure sodium hydrogen carbonate. Sodium carbonate monohydrate was sprayed with 0.5-45% water to make it react into a current of carbon dioxide at appropriate humidity at a temperature of 0-40°C in a 30 litre rotating drum for two hours. The sodium hydrogen carbonate obtained had an impurity of 0.06% sodium carbonate.

Zil'Berman and Aubert [20,21] are among others who attempted to carbonate hydrated sodium carbonate.

It is, thus clear from the previous work done that carbonation of hydrated sodium carbonate to form sodium hydrogen carbonate is practically feasible if the sodium carbonate is hydrated just before use.

However, investigation have not been done on the dependence of absorption of carbon dioxide by the saturated aqueous solution of sodium carbonate or the rate of formation of sodium hydrogen carbonate with respect to pressure and/or temperature. It is of major interest of this work to look into effects of pressure and temperature on the rate and hence yield of absorption of carbon dioxide by sodium carbonate to produce sodium hydrogen carbonate.

CHAPTER THREE

EXPERIMENTAL

3.1 INTRODUCTION

In this section chemicals used, apparatus and experimental procedures are described.

3.2 CHEMICALS

ANHYDROUS SODIUM CARBONATE

This salt was Merck's extra pure for analysis. It was analysed for carbonate according to the methods described later in this section. It was found to be 98.0% pure with impurities of water. It was thus kept in the oven at temperatures 230-250°C throughout the experimental time to avoid more absorption of moisture from the air [21].

SODIUM HYDROGEN CARBONATE

This was also Merck's extra pure salt for analysis. This was found to contain some impurity of normal carbonate of about 3%.

MAGADI SODA (HEAVY SODA)

This was obtained from the Magadi Soda Factory. It is industrially known as Heavy soda.

LIGHT SODA (ANHYDROUS SODIUM CARBONATE)

This is the industrial soda ash. It was obtained from Twiga Chemicals, a subsidiary of Imperial Chemical Industries. They are the local distributors (agents) of Imperial Chemical Industries, hence the owners of Magadi Soda Factory.

SODIUM ACETATE TRIHYDRATE ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$)

This was analar grade obtained from BDH chemical group of United Kingdom.

HYDROCHLORIC ACID

Analar grade concentrated hydrochloric acid was obtained from BDH chemicals (U.K.).

GLACIAL ACETIC ACID

This was analar grade also from BDH Chemical group (U.K.).

SILVER NITRATE

Analar silver nitrate was obtained from May & Baker of the United Kingdom.

CARBON DIOXIDE

Solid carbon dioxide was obtained from carbacid Ltd. so was liquid carbon dioxide which was supplied in Commercial Steel Gas Cylinders.

3.3 INDICATORS

THYMOL BLUE pH 1.2-2.8 and pH 8.0-9.6

This was obtained from BDH laboratory through their local representatives.

CRESOL RED pH 0.2-1.8

This was also obtained from local suppliers of BDH chemicals (U.K.) through their local representatives.

METHYL ORANGE, pH 3.4-5.0 (orange-blue colour)

Hopkin & Williams Ltd. (London) supplied this chemical.

INDIGO CARMINE pH 11.6-14.0

This was supplied by May & Baker of United Kingdom through their local representatives.

POTASSIUM CHROMATE

This was analar grade and was supplied by May & Baker.

POTASSIUM DICHROMATE

This was analar grade and was also supplied by May & Baker.

Mixed indicators to improve the detection of end-point were made as will be explained later in this section.

Distilled water was used throughout the experimental work.

3.4 APPARATUS

3.4.1 pH METER A pH meter of Pye Unicam 292 mK2 model fitted with calomel and glass electrodes was used.

3.4.2 WATER THERMOSTAT

A water bath of dimensions 40x20x30 cm³ was constructed using metal frame (iron bars) and glass panes being affixed with silicone putty (water proof). It was filled with water and fitted with a heating and temperature control unit. It was found to raise the temperature and maintain it within a range of about $\pm 0.1^{\circ}\text{C}$. This was done with the help of a calibrated thermometer.

3.4.3 DENSITY BOTTLE

A density bottle of pyrex glass was used. To achieve good results, it was washed both with water and ethanol and left to dry each time measurements were to be carried out.

3.4.4 AIR THERMOSTAT

An air thermostat of dimensions 80x60x80 cm³ was constructed using perspex sheets mounted on dexion bars. It was lugged from the inside using aluminium paper foil. Three holes were bored at the top to allow the fitting of the temperature control unit and the heating system. Temperatures were adjusted and controlled by an adjustable thermometer which had earlier been calibrated using melting and boiling points of pure water.

The adjustable thermometer was connected to a relay control systems which had a bulb as its heating device. The other bulb, strategically placed in the air thermostat was permanently put on to bring up the temperatures just below the desired temperature. This saved lots of time in raising up temperature. A fan was fitted so as to have even distribution of heat within the thermostat. A small window was made to take in and out samples with ease while avoiding heat loss in case of high temperatures.

3.4.5 FILTER CRUCIBLES

Sintered glass crucibles of porosity number 4 were used. This was the tall form and was adapted to fit various functions. They were of average pore size of 5-10 microns and were used for very fine precipitates. No crystals of sodium hydrogen carbonate or sodium carbonate would go through the pores of these crucibles.

3.4.6 PRESSURIZABLE VESSEL

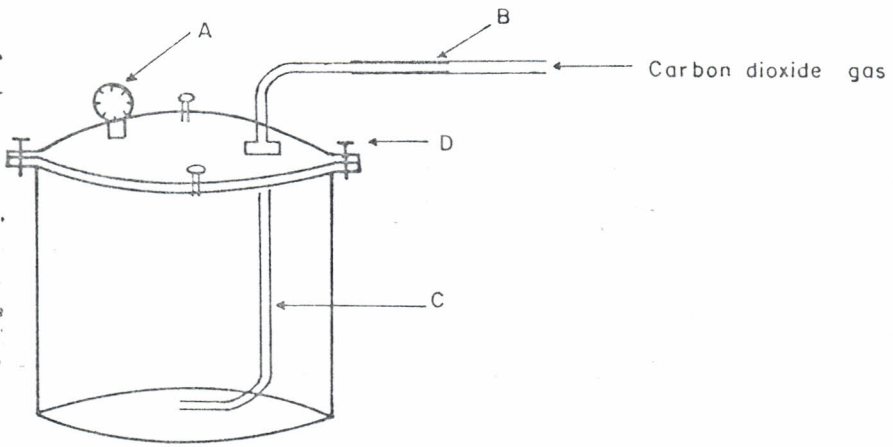
An autoclave made of aluminium and zinc alloy was used for the purpose of raising pressure during the reaction or experimental period while increasing temperature.

An ordinary autoclave was adapted so that a pressure gauge could fit and work well, while having a tubing of copper inserted to introduce carbon dioxide inside the vessel. The gauge was calibrated with the help of several gauges mounted on commercial gas cylinders of various gases. Mostly used, were those of carbon dioxide gas and of oxygen gas. The pressure vessel was such that it could easily be used to work

at a pressure of upto 5 atmospheric pressure. The pressure gauge had a range of 0-8 atmospheric pressures.

DIAGRAM OF THE PRESSURIZABLE VESSEL

DIAGRAM 3.1



- A — Pressure gauge
- B — Rubber tubing
- C — Copper tube inside the vessel
- D — Screws to fasten the lid

3.5 EXPERIMENTAL PROCEDURE

The analysis was done using mixed indicators which were prepared as follows.

3.5.1 MIXED INDICATORS

Two mixed indicators were prepared so as to give a colour change at pH 3.7 for bicarbonate and the other one at pH 8.3 for carbonate.

3.5.1.1 METHYL ORANGE - INDIGO CARMINE MIXED INDICATOR pH 3.7

One gram of methyl orange and 2.5 grams of purified indigo carmine were dissolved in a litre of distilled water and the solution filtered. The colour-change on passing from alkaline to acid solution is from green to magenta with neutral-grey at about pH 4 [21].

3.5.1.2 THYMOL BLUE - CRESOL RED MIXED INDICATOR pH 8.3

Thymol blue - 0.25g of thymol blue in acid form (powder) was dissolved in 100 mls of distilled water in a 250 ml volumetric flask. 5.4 ml of 0.1M sodium hydroxide was added and the solution thoroughly mixed and shaken to dissolve the indicator. It was then diluted upto the mark with distilled water to give a 0.1% aqueous solution of thymol blue sodium salt indicator [21].

Cresol red - 0.25g of cresol red acid form was dissolved in a 250 ml volumetric flask by first adding 6.55 ml of 0.1M sodium hydroxide solution and then diluting and topping it upto the mark with distilled water, with occasional shaking to ensure thorough mixing. This gave a 0.1% aqueous solution of the sodium salt of cresol red.

A mixed indicator was made using the above two solutions in the following manner.

75 ml of 0.1% thymol blue (sodium salt) solution was mixed with 25 ml of 0.1% cresol red (sodium salt) solution to give a mixed indicator of 3 parts of 0.1% thymol blue solution and 1 part of 0.1% cresol red solution of the sodium salt [21].

3.5.1.3 POTASSIUM CHROMATE INDICATOR

42g of (analar) potassium chromate and 0.7g of (analar) potassium dichromate were dissolved in 100 ml of water. It was preferred to use 1 ml of the indicator for 50 ml of the final volume of the test solution. This is so as to maintain the indicator concentration at about 0.005M in the actual titration. This will not affect the endpoint [21].

3.5.2 SOLUTIONS

Various standard solutions were made for analytical work.

3.5.2.1 0.1M STANDARD HYDROCHLORIC ACID

To make approximately 0.1M hydrochloric acid, 8.73 ml pure concentrated hydrochloric acid were measured and poured into one litre volumetric flask half-way filled with distilled water.

It was thoroughly mixed by shaking and brought upto the mark with distilled water.

3.5.2.2 STANDARDISING THE ACID

0.200g of pure sodium carbonate, cooled from the oven, was dissolved in 50 ml of distilled water. Three drops of methyl orange-indigo carmine indicator was added in the conical flask.

The sodium carbonate was titrated against, using the acid until the colour (green) of the indicator changed from pale green to neutral grey. The strength of the acid was computed for each titration and the mean was taken as the strength of the solution.

3.5.2.3 0.1M STANDARD SILVER NITRATE SOLUTION

0.1M silver nitrate solution was made by weighing and dissolving 8.5g of AR silver nitrate (recrystallised) in water and made to 500 ml in a volumetric flask.

3.5.2.4 STANDARDISING THE SOLUTION

2.925g of AR sodium chloride were weighed and dissolved in 500 mls of distilled water in a volumetric flask. This gave a salt solution of 0.100 M sodium chloride solution. 25ml of the solution were pipetted in a conical flask. 1ml of standardized potassium chromate indicator was added. The solution of silver nitrate was run through from the burette, while swirling the liquid constantly until the red colour formed was permanent by the addition of one single drop. This was done slowly and cautiously.

3.5.3 SETTING pH METER

The pH meter was set by the use of buffer solutions. Two buffer solutions of pH 4 and 10, were made [22].

3.5.3.1 BUFFER pH 10

A solution of 0.025M of pure sodium carbonate was made by dissolving 0.625g of sodium carbonate in 250 ml distilled water.

0.025M sodium hydrogen carbonate solution was made similarly, by dissolving 0.525g of pure sodium hydrogen carbonate in 250 ml of distilled water. The two solutions were mixed in equal proportions to give a buffer of pH 10.0.

3.5.3.2 BUFFER pH 4

6.804g of sodium acetate trihydrate were weighed accurately and dissolved in 250 ml of distilled water. This gave a solution of 0.200M sodium acetate.

2.87 ml of glacial acetic acid of density 1.0492g cm^{-3} were dissolved in 250 ml of distilled water to make a solution of 0.200M acetic acid.

41.0 ml of the acetic acid solution were thoroughly mixed with 9.0 ml of 0.200M sodium acetate solution to give a buffer solution of pH 4.0.

The pH meter was calibrated using both solution of known pH values, each time a pH of an unknown solution was to be determined [22].

3.5.4 STANDARDISING MIXED INDICATORS

The colours of the end points for the mixed indicators were verified using known amounts of pure analar samples with the acid and with the help of a pH meter.

3.5 METHYL ORANGE-INDIGO CARMINE MIXED INDICATOR

Known amount of pure AR sodium carbonate was weighed and dissolved in 125 ml of distilled water. The concentration of the solution was now known and also the volume of 0.100M standard hydrochloric acid required to neutralise the solution.

25 ml of the solution were pipetted into a conical flask standing on a magnetic stirrer. The electrodes from the pH meter were put in the solution and the pH meter was switched on. The stirrer was as well switched on. Standard 0.100 M hydrochloric acid was added drop by drop upto the required or calculated amount while watching the pH reading. On reaching the required amount and at pH 3.7, the titration was stopped and three drops of methyl orange-indigo carmine mixed indicator were added. Stirring was continued for sometime till the colour of the solution was homogeneous and well established.

This was taken as the standard colour of endpoint of the indicator for this titration.

3.5.1 THYMOL BLUE-CRESOL RED MIXED INDICATOR

Sodium hydrogen carbonate was treated in a similar way as sodium carbonate above. The titration by standard 0.100 M hydrochloric acid was carried out cautiously till pH 8.3 was reached and simultaneously the theoretical titre volume had been added. The titration was stopped and three drops of thymol blue-cresol red mixed indicator were added. The colour that was attained after a short while of stirring was taken as the standard endpoint colour of thymol blue-cresol red mixed indicator for sodium hydrogen carbonate solutions.

3.6 ANALYSIS

3.6.1 SODIUM CARBONATE

2.700g of pure analar grade sodium carbonate were weighed accurately and dissolved in a 250 mls volumetric flask with distilled water and the volume was brought to the mark with distilled water.

25 ml of the solution were pipetted into a conical flask and titrated against 0.1M hydrochloric acid using methyl orange-indigo carmine mixed indicator. The volume of the titre was taken. This experiment was repeated several times with the same solution and other similar fresh solutions till results were consistent. The consistent titre was used to calculate the percentage of the carbonate in the sodium carbonate calculating the purity of the anhydrous analar grade sodium carbonate.

3.6.2 SODIUM HYDROGEN CARBONATE

2.100g of pure AR sodium hydrogen carbonate were weighed accurately and dissolved in a 250 ml volumetric flask with distilled water with occasional shaking. 25 ml of the solution were pipetted into a flask and was treated the same way as that of sodium carbonate solution using now the thymol blue-cresol red as the indicator. The average or consistent titre was used to calculate the purity of sodium hydrogen carbonate.

3.7 DETECTION LIMIT OF THE ANALYTICAL METHOD

3.7.1 SODIUM CARBONATE

To determine the accuracy of sodium carbonate determination method, solutions of sodium carbonate of various concentrations were made. A stock solution of 1000 ppm sodium carbonate with respect to carbonate was made from which solutions of 100 ppm, 10 ppm, 1 ppm and 0.1 ppm were made by suitable dilutions. Also two solutions of standard hydrochloric acid were made, one of 0.100 M standard hydrochloric acid and the other of 0.010M standard hydrochloric acid. Two solutions of 25 ml each were pipetted into

two conical flasks. One was titrated against 0.100M hydrochloric acid the other 0.010M hydrochloric acid. The same indicator, methyl orange-indigo carmine, was used for both titrations though the quantity in the less concentrated solution was lowered to avoid its acidic effects on the endpoint. The changing of colour range was determined.

3.7.2 SODIUM HYDROGEN CARBONATE

As in the case of sodium carbonate above, solutions of pure analar grade sodium hydrogen carbonate were made. Stock solution of 1000 ppm sodium hydrogen carbonate was made from which solutions of 100 ppm, 10 ppm, 1 ppm and 0.1 ppm were made by suitable dilutions. The two standard hydrochloric acid solutions were used with these solutions which were treated in a similar manner as those of sodium carbonate, only that thymol blue-cresol red mixed indicator was used in second portions of the titrations. The endpoint accuracy or the sharpness of the colour change was determined for each indicator.

3.7.3 LIGHT SODA ASH

3.7.3.1 SODIUM CARBONATE

3.00g of light soda ash were accurately weighed and dissolved in a 250 ml volumetric flask with distilled water. 25 ml of the solution was pipetted into a conical flask and titrated against 0.100M hydrochloric acid using methyl orange-indigo carmine indicator. The volume of the titre named X was recorded and the experiment repeated several times, till there was good agreement among results.

3.7.3.2 SODIUM HYDROGEN CARBONATE

Similar portions were pipetted and titrated against 0.100M hydrochloric acid but this time thymol blue-cresol red indicator was used. The volume of the titre named Y was recorded. This would help in the calculation of sodium hydrogen carbonate content in light soda. The experiment likewise was repeated several times till a constant titre was achieved.

3.7.3.3 SODIUM CHLORIDE

Another similar portion, 25 ml was pipetted into the flask and titrated against 0.100M silver nitrate solution using potassium chromate indicator. This was to test for sodium chloride in the light soda. The experiment was repeated several times until there was a constant titre.

3.7.3.4 SODIUM FLUORIDE

Stock solution of 1000 ppm with respect to sodium carbonate was made. This was analysed for sodium fluoride using the fluoride ion selective electrode.

3.7.4 MAGADI SODA ASH

3.7.4.1 SODIUM CHLORIDE

4.000g of Magadi soda ash were accurately weighed and dissolved in a 250 ml volumetric flask with distilled water. 25 ml of the solution were pipetted into a conical flask and titrated against 0.100M silver nitrate solution using 1 ml of potassium chromate indicator. The titration continued until all of chloride had precipitated and a faint distinct red colour appeared. The experiment was repeated several times until a constant titre was attained.

This was used to calculate the percentage of sodium chloride in the Magadi soda ash.

3.7.4.2 SODIUM CARBONATE

A similar procedure to that carried out for the determination of sodium carbonate in light soda ash was used for determining sodium carbonate in Magadi soda ash. The constant titre attained was used to calculate the percentage of sodium carbonate in Magadi soda ash.

3.7.4.3 SODIUM HYDROGEN CARBONATE

Similarly, the same procedure as the determination of sodium hydrogen carbonate in light soda ash was used for the determination of sodium hydrogen carbonate in Magadi soda ash.

3.7.4.4 SODIUM FLUORIDE

The same was done as in the above case of light soda ash.

3.8 STABILITY STUDIES

3.8.1 SODIUM HYDROGEN CARBONATE

There was need to establish the shelf-life or at what best conditions could sodium hydrogen carbonate be stored. Sodium hydrogen carbonate is known to decompose back to sodium carbonate at temperatures above 60°C or even at some conditions where carbon dioxide can escape from it.

Four samples of pure analar grade sodium hydrogen carbonate were put in four desiccators one in each and at varying conditions. They were left to stand for a period of three months while being analysed weekly.

SAMPLE A

This sample was placed in a dry clean desiccator. Some little amount of water was sprinkled on the sample to make it, just wet. The desiccator was closed and left standing for ten weeks. An aliquot portion of the sample was analysed every week.

SAMPLE B

Sample B was placed under moist conditions at room temperature and pressure. The desiccator had some water at the bottom. Likewise the desiccator with the sample B in it was left standing at room temperature for ten weeks. An aliquot portion of the sample was analysed every week.

SAMPLE C

Sample C was put under moist conditions in a desiccator. Water was put at the bottom of the desiccator. The watch glass containing the sample was placed on top of the desiccator-rack above the water level in the desiccator. The desiccator was then swept with carbon dioxide gas and the tap to the desiccator was closed. The desiccator was left standing for ten weeks. An aliquot portion of the sample was analysed every week while sweeping the desiccator with carbon dioxide each time the lid or tap was opened.

SAMPLE D

Sample D was placed in the desiccator that had as well been cleaned and dried. It was left standing for ten weeks and an aliquot portion of the sample was analysed on weekly basis.

3.8 CARBONIC ACID STABILITY

Carbonic acid is known to be an unstable weak acid. Investigation for its formation and hence stability were carried out in this research work. Double distilled and deionized water of pH 7 was poured into the pressurizable vessel, so as to cover the bottom, horizontally lying tip of the copper tubing. The

lid to the vessel was fastened with help of the screws. The carbon dioxide was introduced through the tubing. The pressure of the vessel was maintained with the help of the regulating cylinder taps. Thus, carbon dioxide was bubbled through the water. The bubbling continued for a given time then stopped. After the vessel's pressure had subsided, the solution of carbonic acid and carbon dioxide dissolved in water was analysed using the pH meter.

Solid carbon dioxide was also used in place of carbon dioxide gas, the only exception was that pressure of the vessel could not be regulated [14].

3.9 SOLUBILITY, DENSITY AND SOLID PHASE DETERMINATION

The solubilities of sodium hydrogen carbonate and sodium carbonate in water and their mutual solubilities were investigated. This was carried out in the water thermostat. The solid phases in equilibria were determined in the air thermostat [22].

3.9.1 SODIUM CARBONATE IN WATER THERMOSTAT

Saturated solutions were obtained in the water thermostat in the following way.

The thermostat was set so as to attain a range of temperatures 20° to 50°C with ease. A boiling tube, fitted with rubber stopper which had been bored at the centre so as to accommodate a stirrer, was immersed in the water bath. The sample of sodium carbonate was put in the boiling tube, distilled water was added and the stirrer was introduced. The boiling tube was immersed to a given level such that all the solution was inside the

bath. The solution's level was below the water level of the bath. This was to avoid heat loss into the air. Stirring was maintained for at least 10 hours.

A solid phase at the bottom of boiling tube was maintained to ascertain a saturated solution. On establishing that no more solid sodium carbonate could dissolve, the saturated solution was analysed.

The stirrer was stopped, withdrawn from the boiling tube and the tube stoppered with an unbored cork while still keeping it immersed in the thermostat for several minutes to one hour for the solid phase to settle.

After the solid had settled a known volume of the solution was filtered off and transferred to a tared weighing bottle. This was done by means of a pipette to the end of which was attached a short glass crucible of filter number G.4 pores by means of a rubber tubing. Due to difficulties in suctioning, a controlled vacuum pump was used.

The solution was weighed and a rough density determination was carried out. It was then poured into a 250 ml volumetric flask and diluted to the mark with distilled water. Volumetric analysis was carried out, as described above, using standard 0.100 molar hydrochloric acid. Its solubility was hence calculated [21].

3.9.2 IN AIR THERMOSTAT

In the air thermostat, temperatures were kept constant similar to those of the water thermostat. The remaining solution in the boiling tube in the water thermostat was quickly decanted on a G.4 crucible that had been adapted to suit our needs

and was placed inside the air thermostat. It had been fastened on to a water vacuum pump for filtration. Care was taken so as not to have solidification during decanting due to heat loss. The filtered solution was divided into two portions.

PORTION ONE:

This portion was poured onto a watch glass and left to dry or solidify in the air thermostat at the same temperature as it had been saturated and filtered. On complete drying, after a day, the solid phase was analysed. The solid was weighed on a scientific weighing balance and then dissolved in distilled water in a 250 ml volumetric flask. The solution was volumetrically analysed for sodium carbonate as in the above analysis of pure sodium carbonate. The weight difference that resulted was believed to be due to water of crystallization [21].

PORTION TWO:

The larger portion, portion two, was filled into a density bottle which had previously been calibrated at that particular temperature, using distilled water. That is to get the exact volume of the distilled water at that particular temperature. Care was taken, to fill the density bottle with the solution, inside the air bath otherwise solidification would occur.

On reaching or leveling to the mark at the given temperature, it was left to cool or adjust to room temperature and was weighed. Density of very good accuracy was determined this way. The results were compared to those of rough determinations done earlier. They were found to be in agreement.

It was necessary to make two to three determinations at a particular temperature. The temperature of both the waterbath

and the air bath were then adjusted to the next temperature of investigation. This was done by raising temperatures at intervals of 4-6°C.

3.9.3 SODIUM HYDROGEN CARBONATE

Sodium hydrogen carbonate (A.R.) was treated the same way as in sodium carbonate above. The only exception was that the vacuum pump was a bit strong and kind-of degassed the warm saturated solution of sodium hydrogen carbonate. It was found to remove the carbon dioxide from the solution hence leaving high concentrations of normal sodium carbonate solution. This * resulted in very high inconsistencies in the saturation or solubility analysis. High contents of sodium carbonate were found.

This type of filtration was avoided and only the water pump products were used.

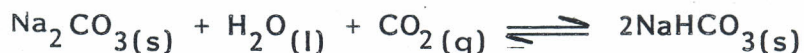
3.10 MUTUAL SOLUBILITIES

After establishing the solubilities of both sodium carbonate and sodium hydrogen carbonate in water, their mutual solubilities were determined. This was done by the same method, only that the solvent was a saturated solution of one of the compound with respect to water. That is, at a particular temperature, a saturated solution of sodium carbonate was attained, this was then used as the solvent, and sodium hydrogen carbonate was dissolved in it till a saturation of sodium hydrogen carbonate was attained. In this particular case, the solubility of sodium hydrogen carbonate in a saturated solution of sodium carbonate was obtained. These conditions were interchanged, varyingly and at various temperatures.

3.11 CARBONATION

3.11.1 LIGHT SODA ASH

The pressurizable vessel was placed inside an air bath for a period of time while containing a given amount of distilled water. On attaining the required temperature a saturated solution of sodium carbonate was made. This had been determined through the solubility studies.



An excess amount of solid carbon dioxide was weighed and put in the vessel and the vessel rapidly closed with the safety screws. Vigorous shaking was effected for the whole of experimental time which lasted three hours. The vessel's pressure was then let to lower down. It was opened and the crystals formed were washed with some little distilled water. The crystals were then dried in the oven at temperatures 60°C and then analysed.

With carbon dioxide gas from the cylinders it was easier to regulate and maintain pressure of the pressurizable vessel at the selected temperature of the air bath. The gas was introduced from the commercial cylinder into the vessel, through a rubber tubing and the copper tubing which went right to the bottom inside the vessel.

First the vessel was set as in the solid carbon dioxide case and a saturated solution made. The vessel's lid was fastened and the taps of the cylinders opened. The pressure gauges both of the vessel and the cylinder were used to regulate the pressure inside the vessel. Shaking as above was effected throughout the

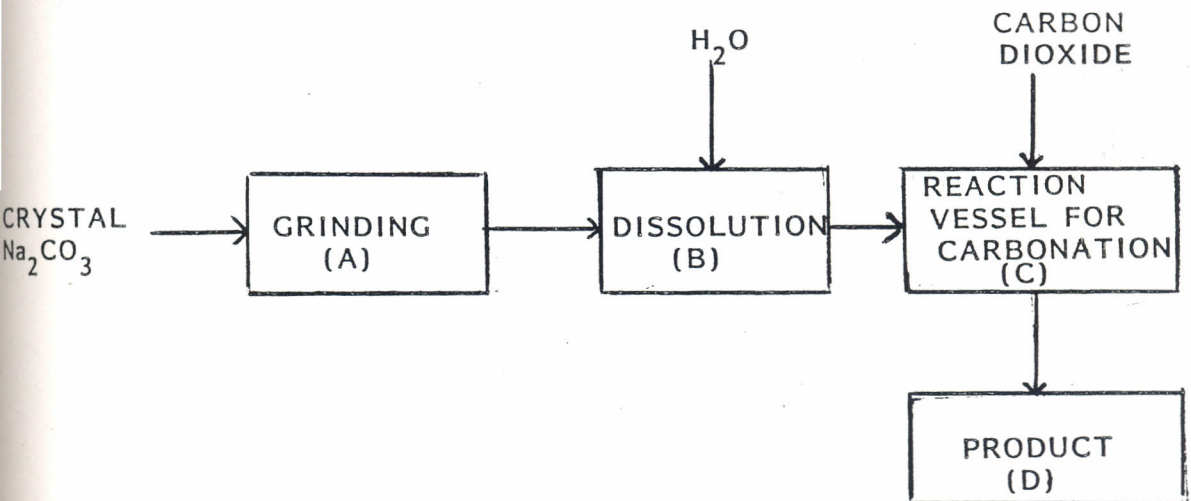
experimental times which was about three hours. The crystals formed were treated as above. The experiments were repeated several times, while increasing the volumes of the saturated solutions, the pressure and the temperatures at intervals similar to those done during solubility studies.

3.11.2 MAGADI SODA ASH

Magadi soda ash was treated the same way as the light soda ash. Only that it had to be ground further before weighing so as to have an easier or faster dissolution of solid in the distilled water.

In general the carbonation process used in this work can be described in the following manner (Schematic diagram).

UNIT PROCESSING DIAGRAM



3.11.3 OPERATIONAL DESCRIPTIONS

- (a) Sodium carbonate crystals were ground to fine powder.
- (b) The powdered sodium carbonate was dissolved in a given amount of water at a selected temperature to make a homogeneous saturated solution.
- (c) The saturated solution was put in the vessel and carbonation was effected at selected temperature and pressure.
- (d) The product sodium hydrogen carbonate separated out and was washed with distilled water, dried at a selected temperature and analysed for yield and purity.

The carbonation was carried out 20 times.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 DETECTION LIMIT

4.1.1 SODIUM CARBONATE

The titrations of sodium carbonate were carried out using 0.1M hydrochloric acid and methyl orange-indigo carmine mixed indicator. Different concentrations of the sodium carbonate solution were analysed so as to establish the lowest concentration that could be analysed using this analytical method. The results are given below in Table 4.1.

TABLE 4:1 TITRATION OF SODIUM CARBONATE WITH HYDROCHLORIC ACID.

Na ₂ CO ₃ (s) (g) DISSOLVED IN 250 ml OF H ₂ O	ANALYTE (ml)	CONCENTRATION OF CARBONATE (PPM)		DEVIATION %
		THEORETICAL	EXPERIMENTAL	
0.4417	20	1000	990.6	+0.9
0.4417	25	1000	995.2	+0.5
0.0442	20	100	113.2	-13.2
0.0044	25	10	11.3	-13.2
0.8834	25	2000	1992.5	+0.4
0.8834	20	2000	2009.4	-0.5
0.0884	20	200	200.2	-0.1
0.8834	50	2000	2000.4	-0.0
0.0044	50	10	10.2	-1.9

From table 4:1 the percentage error increased with reduced amount of carbonate dissolved. The lower the concentration the higher the percentage error. However with higher volumes of low concentrations, a much lower percentage error was attained. The percentage error of a 10 ppm solution was improved from -13.2% to -1.9% by using double the amount of analyte. This is an 85.7% improvement.

4.1.2 SODIUM HYDROGEN CARBONATE

The detection limits of sodium hydrogen carbonate were determined using 0.1M hydrochloric acid being titrated against two solutions of the same amount and concentrations. To one solution, three drops of thymol blue-cresol red mixed indicator were added, to detect endpoint due to carbonate only. To the other solution methyl orange-indigo carmine mixed indicator was used for hydrogen carbonate and carbonate together.

The hydrogen carbonate concentration was then calculated.

Table 4:2 below shows the results of titrations of sodium hydrogen carbonate.

TABLE 4:2 TITRATION OF SODIUM HYDROGEN CARBONATE WITH 0.1M HCl.

Na ₂ CO ₃ (s) DISSOLVED IN 250 ml OF H ₂ O	ANALYTE (ml)	CONCENTRATION OF HYDROGEN CARBONATE IN PPM		DEVIATION %
		THEORETICAL	EXPERIMENTAL	
0.3443	20	1000	980.4	+2.0
0.3443	25	1000	987.6	+1.3
0.0344	25	99.9	87.1	+12.8
0.0034	25	9.9	14.5	-47.0
0.0068	25	19.8	20.3	-3.0
0.0344	50	99.9	101.7	-1.8
0.0034	50	9.9	10.2	-2.9

The percentage error in the titration of sodium hydrogen carbonate increased with decrease in the amount of sodium hydrogen carbonate dissolved in 250 ml of water. Results were improved by using large volumes of low concentrations. A solution of 10 ppm improved the percentage error from -47 to -2.9 by doubling the volume.

A perusal of the data in tables 4:1 and 4:2 shows that concentrations of 10 ppm of both sodium carbonate and sodium hydrogen carbonate could easily be detected. The percentage error for both salts was 3%. Concentrations of 1 ppm of both salts gave problems in their analysis due to failure of establishing their endpoint exactly. However, a concentration of 10 ppm of any of the salts in this work is considered low enough. This is because, in the conversion of sodium carbonate to sodium hydrogen carbonate or in the

solubility studies of both salts, the concentrations involved were much higher.

For example in the conversion



When the conversion gave 40% yield for a 200g starting sodium carbonate solid, then 80g of sodium carbonate will be converted leaving 120g of sodium carbonate in solution. This is a concentration of 67,924.5 ppm. The sodium hydrogen carbonate formed is 92,075.5 ppm. Hence a concentration of 10 ppm is low compared to the solutions in question in this work.

4.2 PURITY DETERMINATIONS

4.2.1 SODIUM CARBONATE

The laboratory analar grade sodium carbonate was analysed for carbonate. The analysis was carried out 20 times using 0.10M hydrochloric acid and methyl orange-indigo carmine mixed indicator and a pH meter. The purity of the salt was found to be 98.1% with a standard deviation of 0.3%. The main impurity was found to be moisture. To improve on this the sample was constantly kept in an oven at a temperature of 250°C. Temperature beyond this would decompose the salt. Drying the sodium carbonate improved the purity to 99.2% with a standard deviation of 0.3%. The dried sodium carbonate was used for all the other experiments.

4.2.2 SODIUM HYDROGEN CARBONATE

The analar reagent was analysed for hydrogen carbonate. The analysis was carried out 20 times using 0.10M hydrochloric acid,

methyl orange-indigo carmine mixed indicator, thymol blue-cresol red mixed indicator and the pH meter. The purity of sodium hydrogen carbonate was found to be 97.2% with a standard deviation 0.2. The impurities included sodium carbonate and moisture. Although it was possible to reduce the moisture content by drying the salt at 70°C, this was found to increase the carbonate content. The sodium hydrogen carbonate was therefore used as purchased, making allowances to the small percentage of impurities in any calculations.

4.2.3 LIGHT SODA ASH

Light soda ash was analysed 20 times for sodium carbonate, sodium hydrogen carbonate, sodium chloride and sodium fluoride. It was found to contain 97.0% (0.1% standard deviation) of sodium carbonate. This compares well with that of the analar grade. The sodium chloride content was found to be 0.8% (0.0% standard deviation). The soda ash was also found to contain some sodium hydrogen carbonate. The hydrogen carbonate content was found to be 0.8%.

The fluoride ion content in the light soda ash was found to be less than 0.1% while using the fluoride ion selective electrode.

4.2.4 MAGADI SODA ASH

Magadi soda ash was analysed 20 times in a similar manner as light soda ash. It was analysed for carbonate, hydrogen carbonate, chloride and fluoride respectively. The carbonate in magadi soda ash was found to be 96.7% (S.D. 0.5%). This was the same as in light soda ash. The chloride content was 0.9% (S.D. 0%). This

was slightly higher than in light soda ash. Magadi soda ash occurs naturally as trona which contains sodium chloride among other salts. The hydrogen carbonate was found to be 0.8% (S.D. 0%) of Magadi soda ash. This correspond well with the hydrogen carbonate content in light soda ash. Fluoride content was 0.8% (S.D. 0.0%). This was higher than in light soda ash.

4.3 SOLUBILITY

4.3.1 SODIUM CARBONATE

Solubility graph of sodium carbonate in water is presented in Figure 4.1.

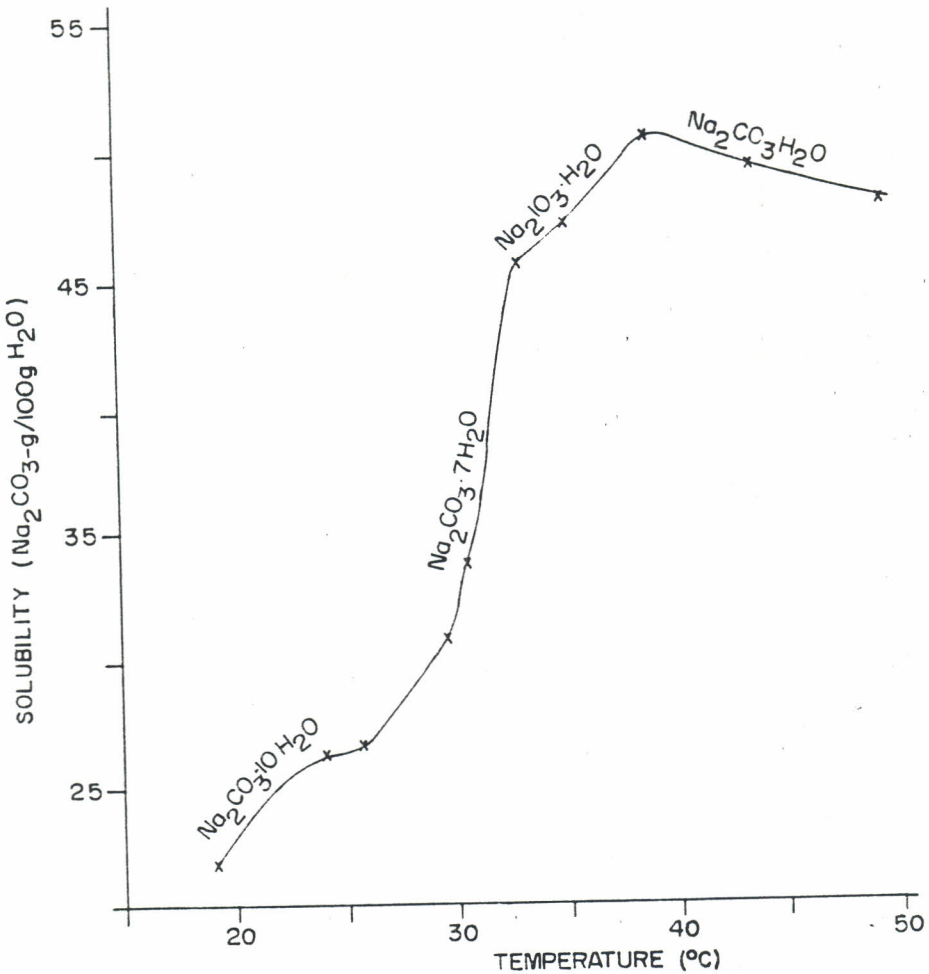


FIGURE 4.1: SOLUBILITY OF SODIUM CARBONATE

The solubility increases sharply upto a temperature of 39°C and then decreases gradually at higher temperature. The curve, however is not smooth. This is due to various solid phases which are in equilibrium with the saturated solution at particular temperatures.

Between temperatures 20°C and 30°C the solid phase in equilibrium with the salt solution is the sodium carbonate decahydrate. From temperatures 33°C to 37°C sodium carbonate heptahydrate is at equilibrium with the salt solution. Sodium carbonate monohydrate exists between 37°C and 50°C . There are transition points where both hydrates will appear. These are at temperatures when one hydrate is changing to another.

The density plotted against temperature resembles the solubility curves. Figure 4.2 is a plot of density of solution against temperature. The solid phases at equilibrium with the solution also correspond to those of solubility curve.

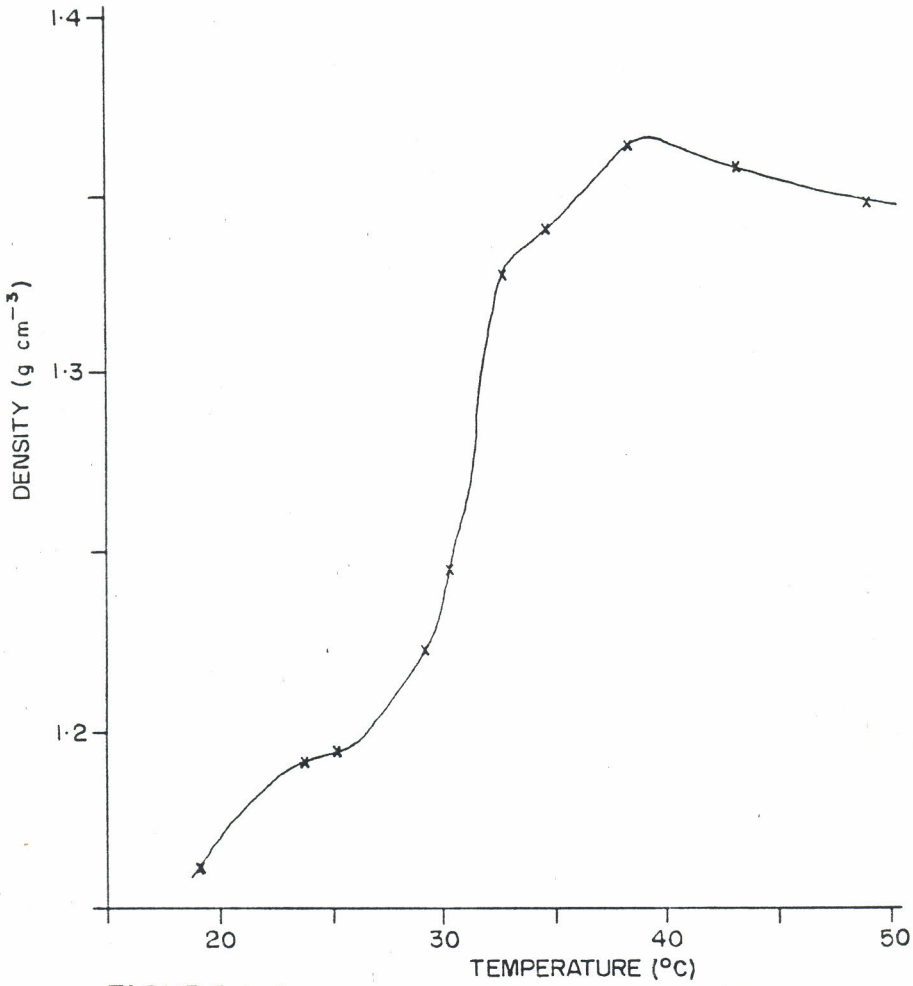


FIGURE 4.2: DENSITY VS TEMPERATURE OF SODIUM CARBONATE

A plot of density against solubility gave a straight line graph. This is presented in Figure 4.3.

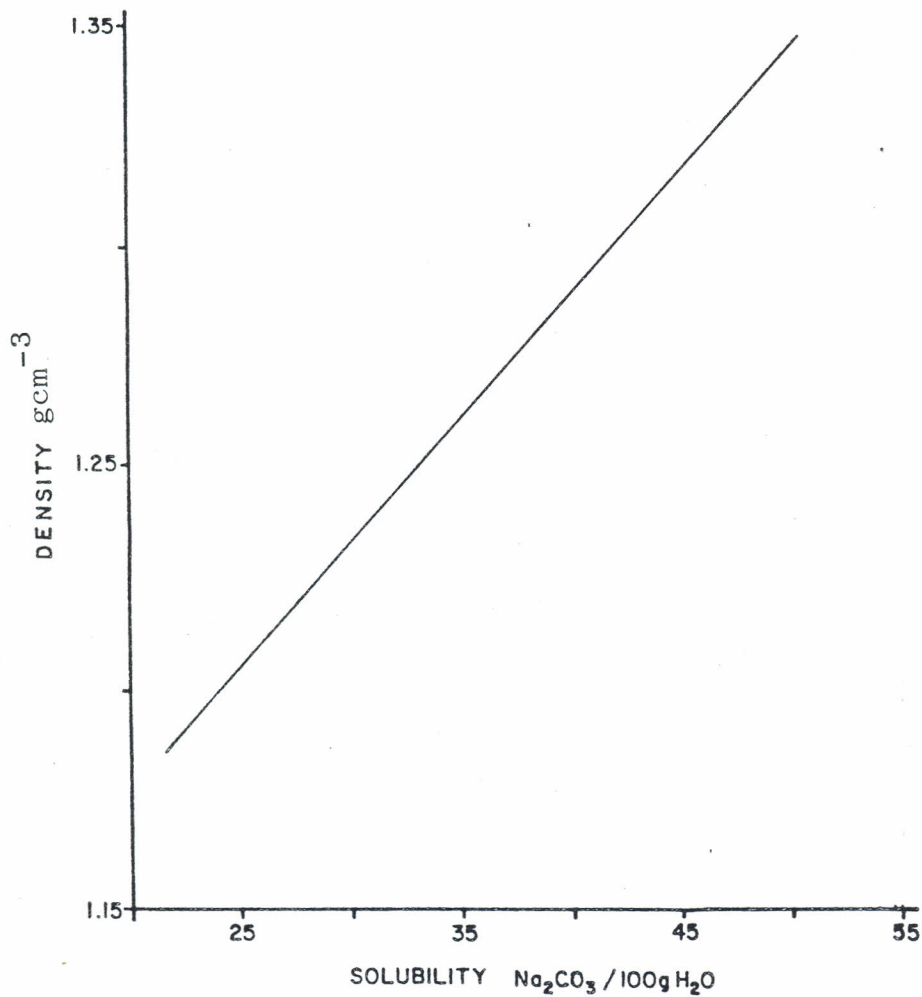


FIGURE 4.3 : DENSITY Vs SOLUBILITY OF SODIUM CARBONATE

The graph shows that there is a direct relationship between the solubility and density of the solution. From the equation of line graph

$y = mx + c$ one can calculate the density of a particular solution, if the solubility of that solution, at that particular temperature is known. The gradient "m" for this graph has been found to be 5.66×10^{-3} while the y- intercept is 1.06 g cm^{-3} . The y-intercept is the density when no solid has been dissolved hence it corresponds to density of pure water.

The relationship between density and solubility for a given solution may be expressed as:

$$\delta = 5.66 \times 10^{-3}S + 1.06$$

where S = solubility

δ = density

The solubility values obtained in this work correspond well with those sited in some literature, only that some solubility values were higher. The largest solubility value occurs at 35°C in the literature while it occurs at 40°C in this work. Figure 4:4 presents a graph of solubility from Seidel [25].

4.3.2 SODIUM HYDROGEN CARBONATE

Results of solubility of sodium hydrogen carbonate in a 100g of water are presented in Figure 4:5 curve 1. The solubility curve rises gradually with increase in temperature.

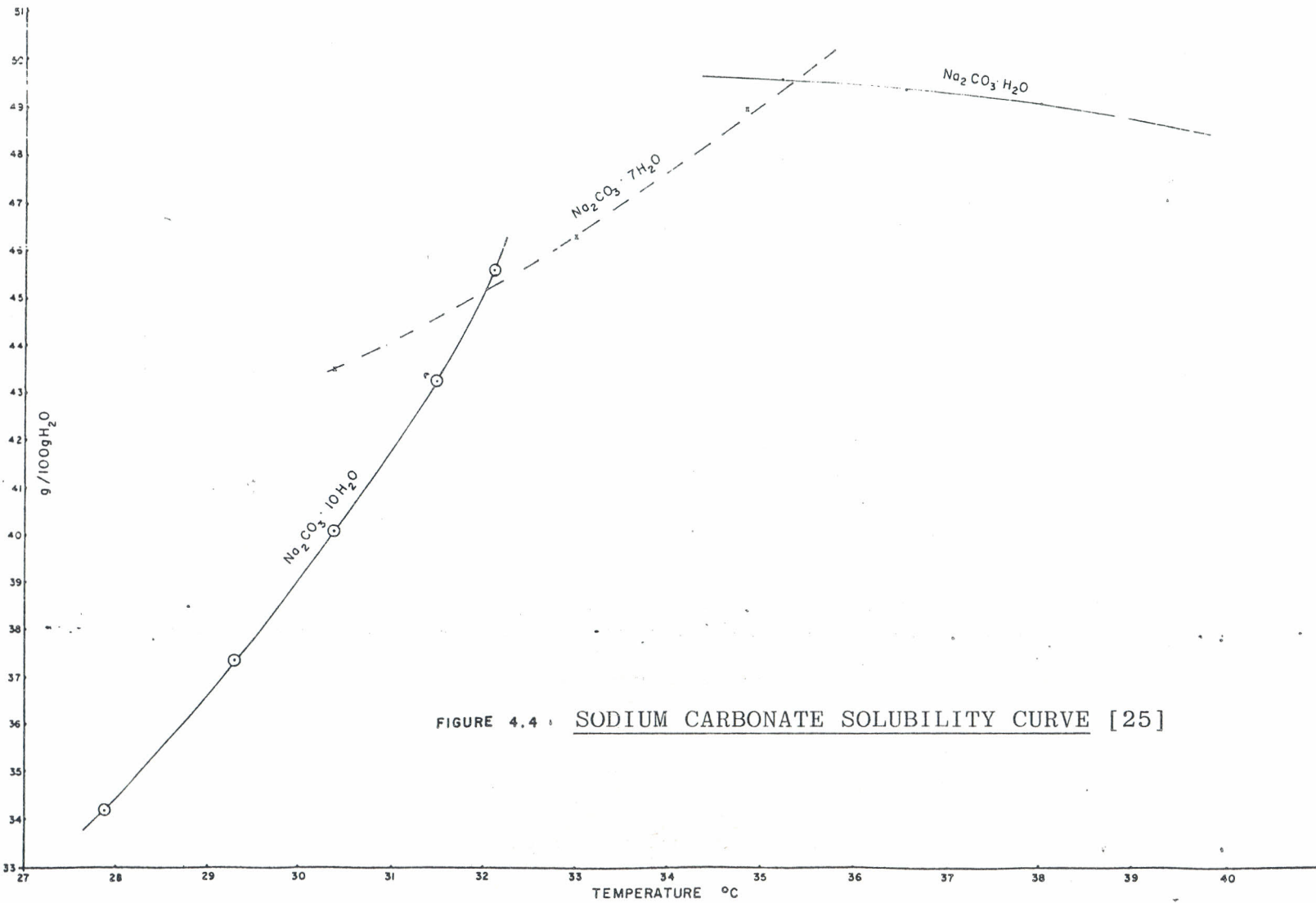


FIGURE 4.4 : SODIUM CARBONATE SOLUBILITY CURVE [25]

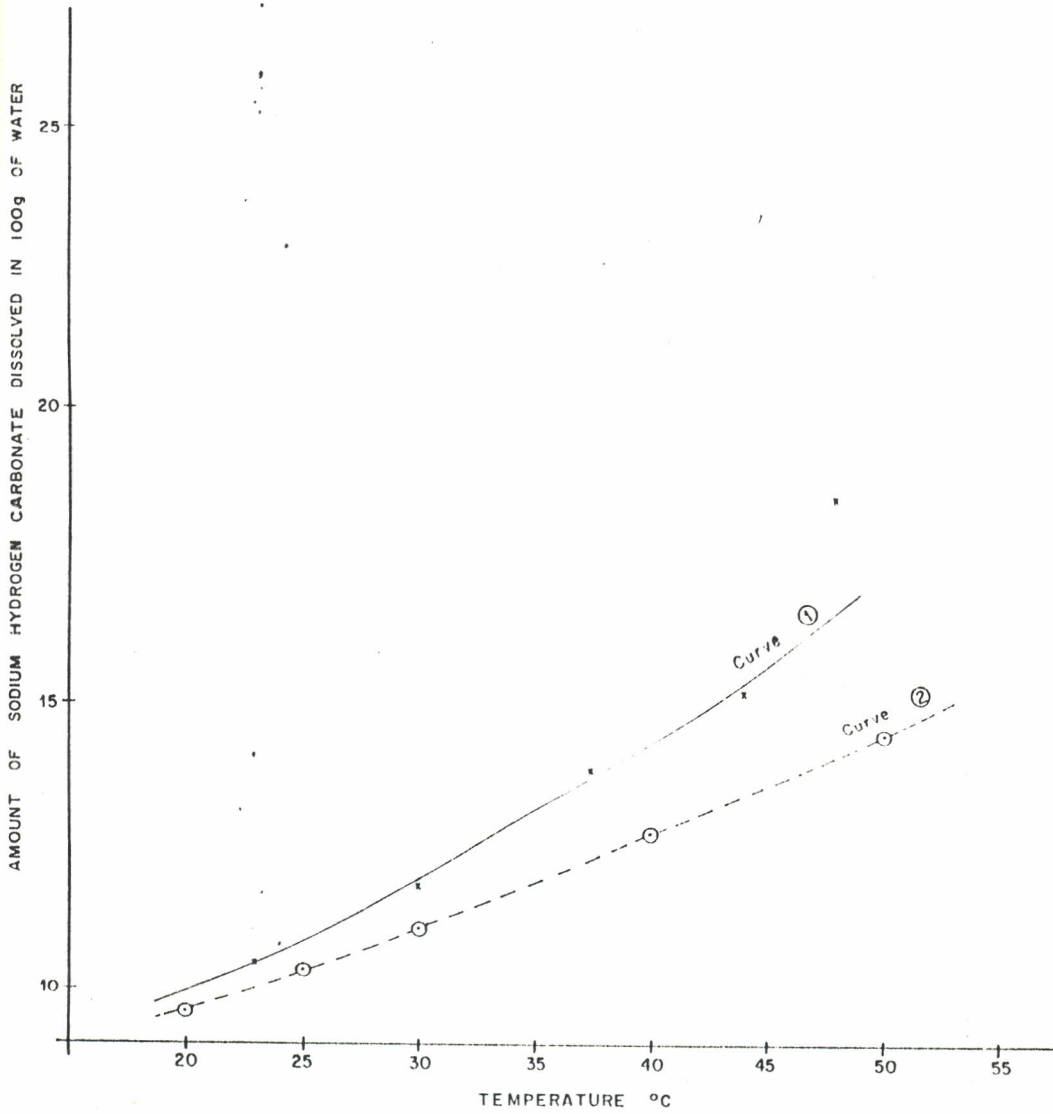


FIGURE 4.5 : SOLUBILITY OF SODIUM HYDROGEN CARBONATE

Curve 1 : Experimental results .

Curve 2 : Siedels solubility results (25)

The solid phase in equilibrium with the salt solution is sodium hydrogen carbonate. However, traces of sodium sesquicarbonate were detected in samples of sodium hydrogen carbonate at temperatures of about 35°C to 50°C when cooled to room temperature during analysis. Sodium sesquicarbonate is formed when a given proportion of sodium carbonate and sodium hydrogen carbonate at temperatures of about 40°C is cooled to room temperature.

A plot of density of sodium hydrogen carbonate saturated solution against temperature was plotted and presented in Figure 4:6.

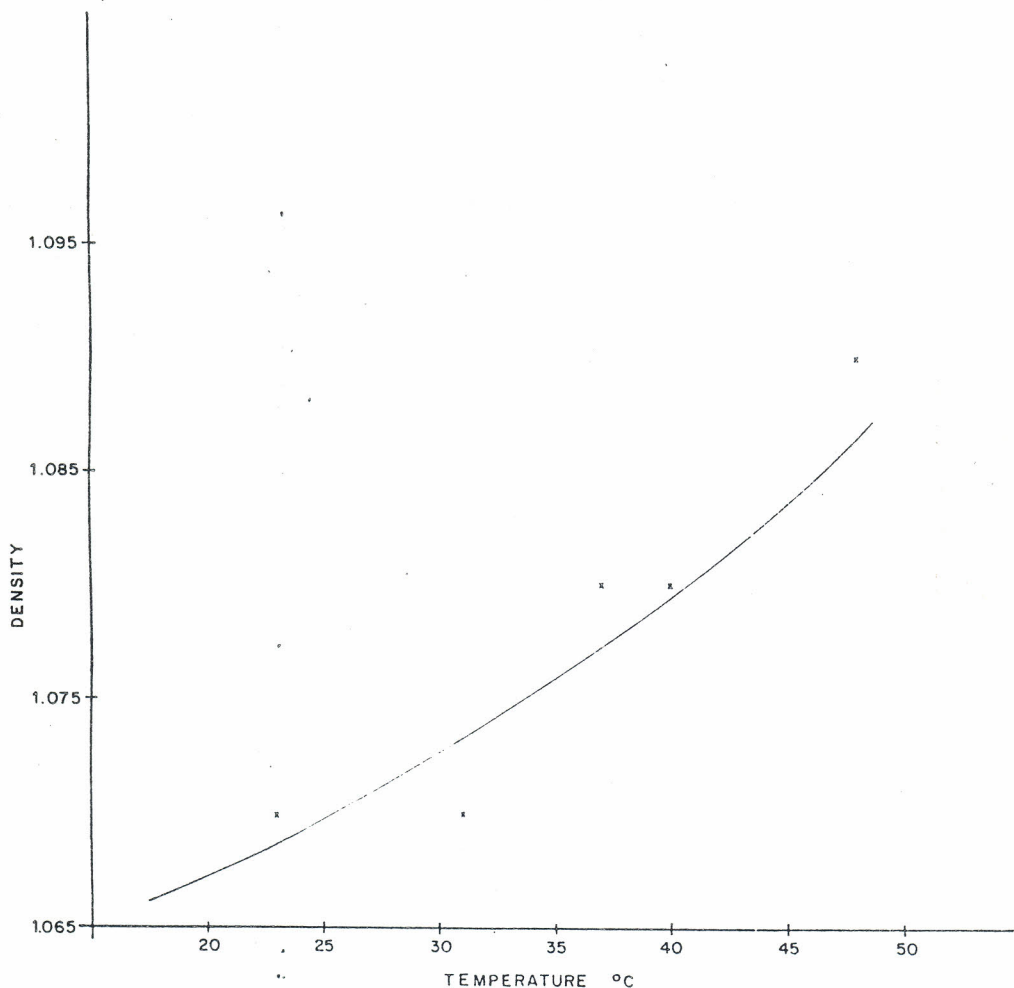


FIGURE 4.6 DENSITY OF SODIUM HYDROGEN CARBONATE AGAINST TEMPERATURE

The graph resembles the solubility curve of sodium hydrogen carbonate obtained earlier.

On plotting density against solubility showed a direct relationship, this is presented in Figure 4:7.

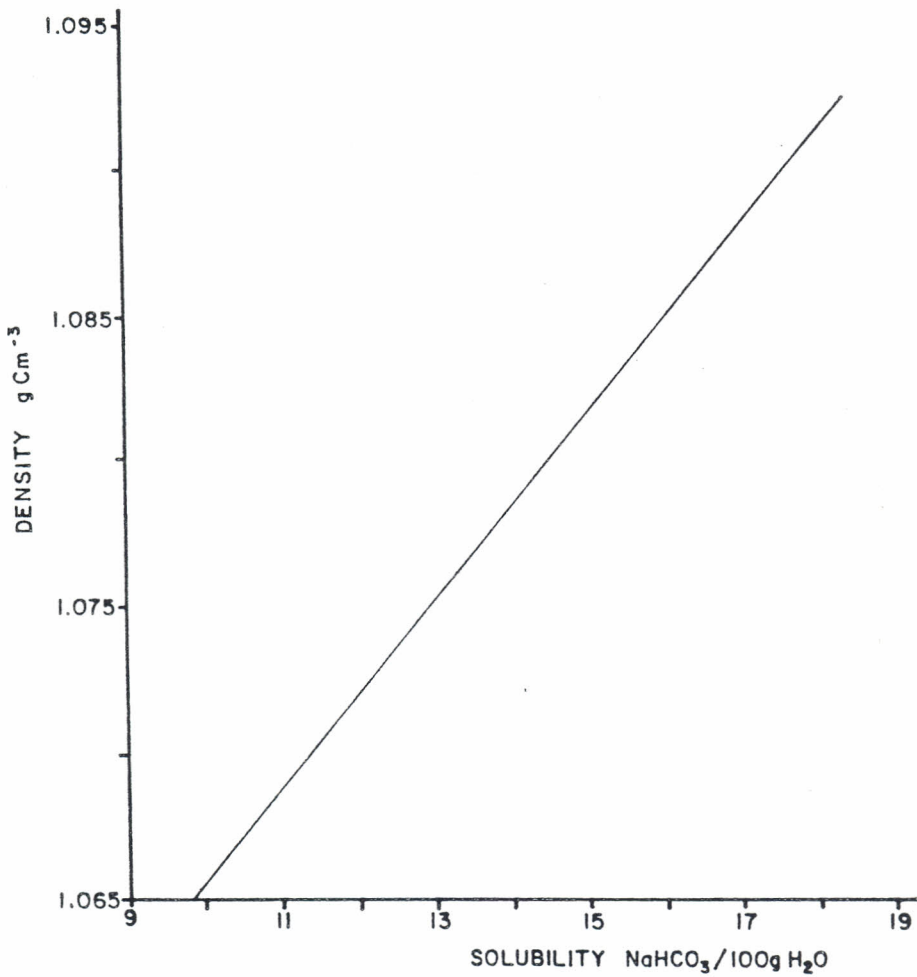


FIGURE 4.7 : DENSITY Vs SOLUBILITY OF SODIUM BICARBONATE

This is a straight line graph with a general equation $y = mx + c$. The gradient 'm' is the direct proportionality constant which is obtained from the graph.

This was found to be 3.3×10^{-3} . The y-intercept 'c' represents the density of the solution when no solid has been dissolved. This was found to be 1.03 g cm^{-3} . This value corresponds to the density of pure water. The relation obtained from the graph is $\delta = 3.3 \times 10^{-3}S + 1.03$

δ = density of sodium hydrogen carbonate solution

S = solubility of sodium hydrogen carbonate solution

That is, given either solubility or density of a particular solution, one is able to calculate the other.

The solubility results of sodium hydrogen carbonate obtained were slightly higher than those sited in most literature. In Figure 4:5, curve 2 presents siedels solubility results [25]. The difference of the two curves increases with increase in temperature. This could have been due to some sodium hydrogen carbonate changing to sodium carbonate in solution due to high temperature and stirring [27]. At higher temperatures, above 35°C a trace of sodium carbonate was detected.

4.3.3 MUTUAL SOLUBILITY

Mutual solubility is the solubility of a particular solid in a solution of another solid. The mutual solubility of sodium carbonate is the solubility of sodium carbonate in an aqueous solution of sodium hydrogen carbonate of a given concentration. These experiments were done to enable us to

understand the separation of sodium hydrogen carbonate from a solution of sodium carbonate. The mutual solubilities of the salts are presented below in tabular form.

Table 4:3 shows the results of mutual solubility of sodium hydrogen carbonate in a saturated solution of sodium carbonate in water.

TABLE 4: 3 MUTUAL SOLUBILITY OF SODIUM HYDROGEN CARBONATE IN AN AQUEOUS SOLUTION OF SODIUM CARBONATE.

TEMPERATURE (°C)	SOLUBILITY OF Na_2CO_3 IN H_2O (g/100g H_2O)	SOLUBILITY OF NaHCO_3 IN 100g Na_2CO_3 SATURATED SOLUTION
20	22	0.30
25	31	0.30
30	41	0.32
35	45	0.31
37	49	0.29
39	50	0.24
41	51	0.22
45	49	0.21
50	47	0.23

The mutual solubility of sodium hydrogen carbonate in a saturated solution of sodium carbonate decreases slightly with increase in temperature.

Results of mutual solubility of sodium carbonate in a saturated solution of sodium hydrogen carbonate are presented in Table 4:4 below.

TABLE 4:4 MUTUAL SOLUBILITY OF SODIUM CARBONATE
IN AN AQUEOUS SOLUTION OF SODIUM
HYDROGEN CARBONATE

TEMPERATURE (°C)	SOLUBILITY OF NaHCO ₃ IN H ₂ O (g/100g H ₂ O)	SOLUBILITY OF Na ₂ CO ₃ IN 100g NaHCO ₃ SATURATED SOLUTION
20	9.89	1.40
25	10.71	1.52
30	12.01	2.03
35	13.20	2.41
37	14.10	3.07
39	14.72	4.04
41	14.75	4.20
45	16.80	4.63
50	18.50	5.20

Solubility of sodium carbonate in a saturated solution of sodium hydrogen carbonate in water was difficult to determine as sodium hydrogen carbonate in solution was converted to sodium carbonate upon stirring for a long time and at temperatures above 30°C. This is reflected in the high solubility figures in table 4:4. Moreover the equilibrium



is favoured by heat, vigorous stirring and such parameters that shift the equilibrium to the right.

4.4 STABILITY OF SODIUM HYDROGEN CARBONATE

Results of stability of the sodium hydrogen carbonate are given below in tables 4:5 to 4:8.

Table 4: 5 presents the results of sample A. Sample A was made wet and left in dry air at normal room temperature inside a dry, clean desiccator. The sample was left for a period of ten weeks and analysed weekly.

TABLE 4:5 RESULTS OF SAMPLE A

WEEK	AMOUNT OF A IN GRAMS	% H ₂ O IN SAMPLE A	% NaHCO ₃ IN SAMPLE A	% Na ₂ CO ₃ IN SAMPLE A
0	0.306	3	90	3
1	0.301	4	85	10
2	0.321	6	80	13
3	0.307	7	79	13
4	0.323	6	78	15
5	0.325	8	75	15
6	0.334	10	70	14
7	0.306	12	71	15
8	0.308	13	70	15
9	0.330	14	70	15
10	0.298	14	70	15

Apart from the little amount of carbonate present in the sodium hydrogen carbonate, more of the carbonate was formed under these conditions. The percentage of the carbonate formed stabilized in the fourth week. This is attributed to the stabilizing of the equilibrium of sodium hydrogen carbonate to carbon dioxide in the enclosed desiccator. The wetness of the sample which slowly turned to almost a complete solution was responsible for the shift of the equilibrium. The sample dissolved in its wetness due to the higher solubility of sodium carbonate formed as compared to sodium hydrogen carbonate and the water formed due to the shift of the equilibrium to the right.



Results on Sample B are presented in table 4:6. Dry Sample B was placed under moist conditions in a desiccator. The desiccator was left standing at room temperature and one atmospheric pressure.

TABLE 4: 6 RESULTS OF SAMPLE B

WEEK	AMOUNT OF SAMPLE B IN GRAMS	% H ₂ O IN SAMPLE B	% NaHCO ₃ IN SAMPLE B	% Na ₂ CO ₃ IN SAMPLE B
0	0.4000	0	97	3
1	0.4008	1	94	5
2	0.4124	2	91	7
3	0.4098	4	88	8
4	0.4007	5	85	10
5	0.4034	6	84	10
6	0.4039	6	83	11
7	0.4020	7	81	12
8	0.4010	8	79	13
9	0.4100	8	79	13
10	0.4079	8	79	13

Sample B behaved in the same way as Sample A. The only difference being that Sample B had a gradual change as compared to Sample A. This is because of the moist condition, or the water placed at the bottom of the desiccator to collect on the watch glass so as to moisten and dissolve the sample. As in Sample A, the moist conditions shifted the equilibrium to the right. The carbon dioxide gas formed prevented further conversion of sodium hydrogen carbonate to sodium carbonate. The sample dissolved in the wetness due to the same reasons as in sample A. However, the wetness in this case increased since there was a continuous source of water (bottom of desiccator) hence increasing the percentage of water and reducing simultaneously both salts' percentages in any aliquot portion of the sample analysed.

Results of sample C are presented in table 4:7. Sample C was placed in moist conditions, by placing water at the bottom of the desiccator. The desiccator was then swept with carbon dioxide gas and left to stand for a period of ten weeks. An aliquot portion of the sample was analysed weekly and each time the desiccator was swept afresh with carbon dioxide gas.

TABLE 4:7 RESULTS OF SAMPLE C

WEEK	AMOUNT OF SAMPLE C IN GRAMS	% H ₂ O IN SAMPLE C	% NaHCO ₃ IN SAMPLE C	% Na ₂ CO ₃ IN SAMPLE C
0	0.3677	0.0	97.0	3.0
1	0.3675	1.0	96.0	3.0
2	0.3523	2.0	95.5	2.5
3	0.3708	4.0	94.0	2.0
4	0.3700	6.0	92.0	2.0
5	0.3698	7.2	90.1	1.9
6	0.3689	9.0	89.5	1.5
7	0.3701	10.5	88.0	1.5
8	0.3721	13.4	85.3	1.3
9	0.3545	15.3	83.6	1.3
10	0.3685	16.0	82.8	1.2

Sample C was found to contain 3.0% of normal carbonate. The sample dissolved in the moisture that collected on the watch glass. The collection of water on the watch glass in the desiccator depended on the temperatures of the day to vapourize the water and then condense it. The equilibrium was held constant as can be inferred from the table. Both sodium hydrogen carbonate and sodium carbonate reduced in percentage for all aliquot portion of samples analysed as the water content increased. The moist conditions were prevented by the carbon dioxide in the desiccator from shifting the equilibrium.

Results on Sample D are presented in Table 4: 8 .

Sample D was placed in a clean dry dessicator at room temperature and pressure and left standing for a duration of ten weeks.

TABLE 4: 8 RESULTS OF SAMPLE D

WEEK	AMOUNT OF SAMPLE D IN GRAMS	% NaHCO ₃ IN SAMPLE D	% Na ₂ CO ₃ IN SAMPLE D
0	0.3889	97.0	3.0
1	0.3834	97.0	3.0
2	0.3803	97.0	3.0
3	0.3848	97.0	3.0
4	0.3815	97.0	3.0
5	0.3867	97.0	3.0
6	0.3941	97.0	3.0
7	0.3796	97.0	3.0
8	0.3843	97.0	3.0
9	0.3850	97.0	3.0
10	0.3872	97.0	3.0

It can be deduced from table 4:18 that the sample did not change. The sample was not placed under moist conditions to induce shifting of the equilibrium. There could have been an increase in temperature or some moisture in the storage of the original sample for it to have attained same amount of carbonate.

The above results show that sodium hydrogen carbonate is best stored in dry place and at room temperature under an atmosphere of carbon dioxide gas. This will prevent shifting of equilibrium to form sodium carbonate and water that will further push the equilibrium to the right.

4.5 CARBONATION

4.5.1 LIGHT SODA ASH

Results of the carbonation of light soda ash at various conditions are presented in graphical form below.

Light soda ash was carbonated both in the air bath and in water bath. Solid carbon dioxide as well as carbon dioxide gas were used in the establishment of the optimum temperatures, pressure and time for carbonation. The figures 4.8, 4.9, 4.10 below present plots of yield against these parameters.

Figure 4.8 presents a plot of yield against temperature at constant pressure of two atmosphere and three hours of carbonation.

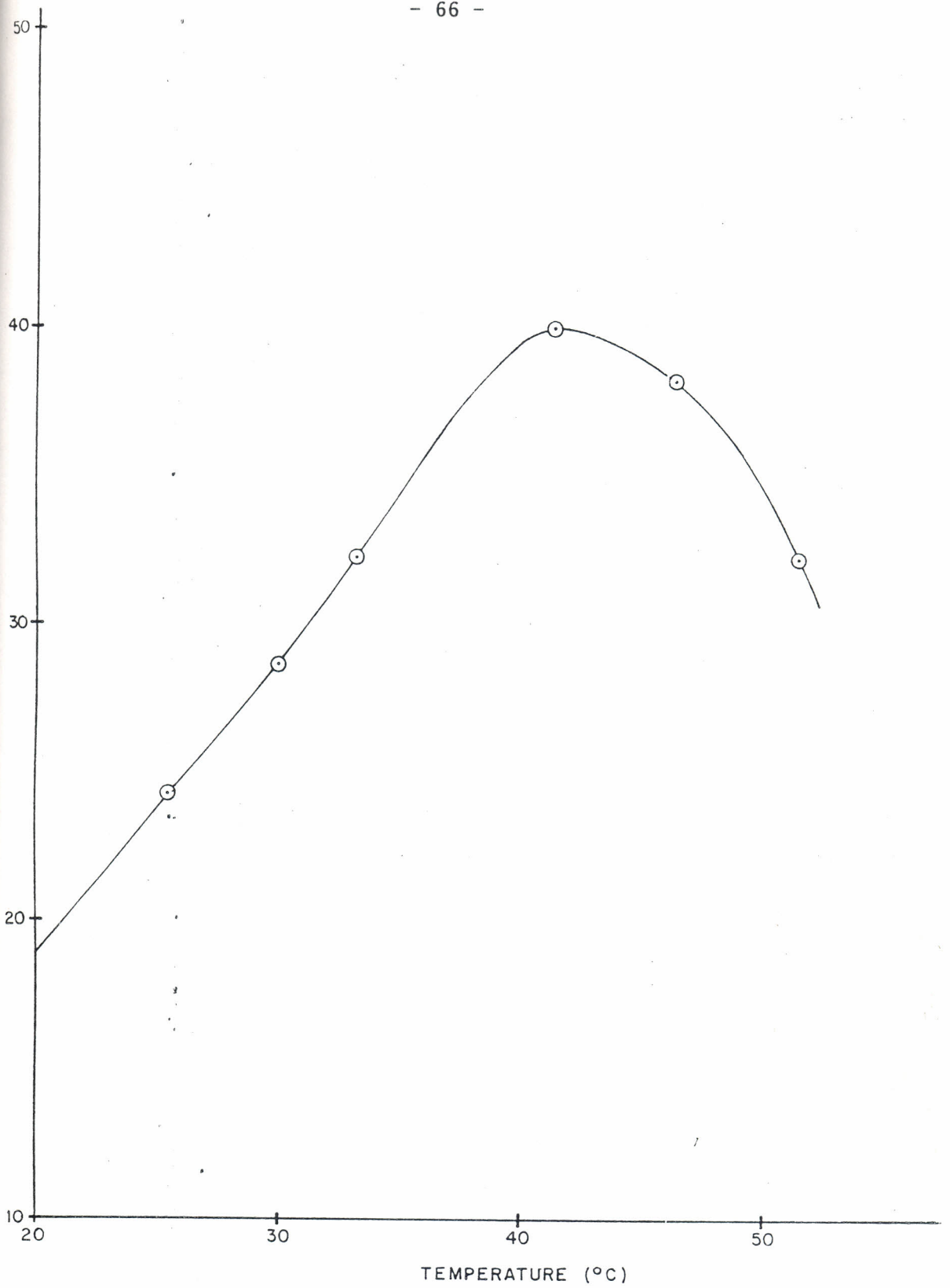


FIGURE 4.8 : YIELD OF SODIUM HYDROGEN CARBONATE AGAINST TEMPERATURE AT TWO ATMOSPHERIC PRESSURE.

An optimum temperature of 40°C was established with a yield of 40%. This temperature corresponds to the temperature of highest solubility of sodium carbonate. At this temperature the solubility difference between sodium carbonate and sodium hydrogen carbonate is 35.5g/100g H₂O, being the largest than at any other temperature. Therefore, the sodium hydrogen carbonate formed will separate out more easily [9]. The results obtained on using either air or water bath corresponded quite well. However, in the airbath, the vessel took longer time to adjust to the bath's temperature. It was easier to shake the vessel while in the air bath than in the water bath.

Figure 4:9 presents results of carbonation of light soda ash at a constant temperature of 40°C and a constant pressure of 2.5 atmosphere at various time intervals. Curve 1 represents carbonation using carbon dioxide gas while curve 2 shows carbonation using solid carbon dioxide.

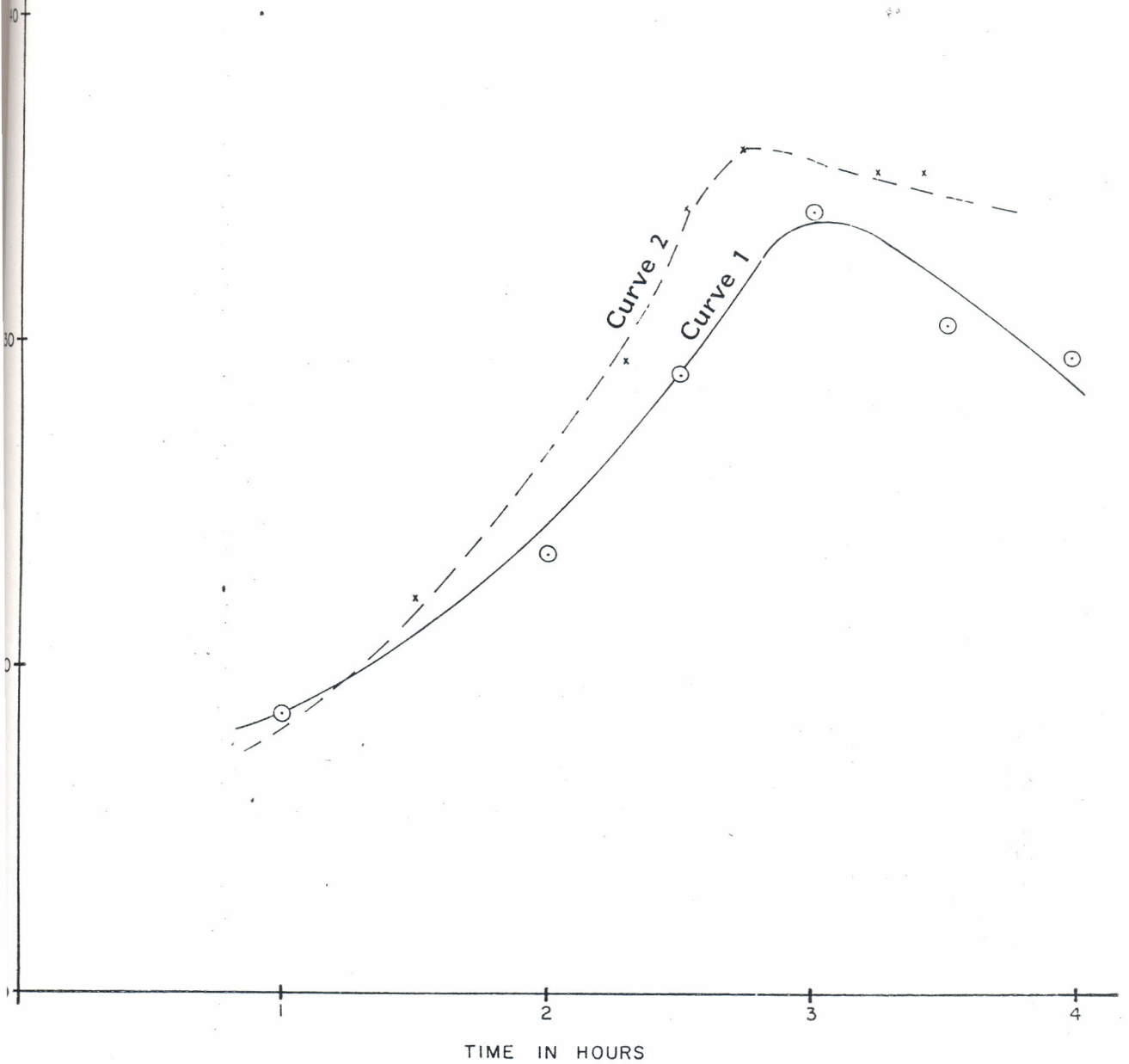


FIGURE 4.9 : YIELD OF SODIUM HYDROGEN CARBONATE AGAINST TIME AT A TEMPERATURE OF 40°C AND PRESSURE OF 2.5 ATMOSPHERIC PRESSURE.

From the plot it can be deduced that for the first three hours, the yield increased with increase in time. Beyond three hours, most of the carbon dioxide gas put in was found to leak out therefore reducing the percentage yield. Solid carbon dioxide gave better yields with less time than with carbon dioxide gas as shown in Figure 4:9 curve 2. However, carbon dioxide solid posed a problem of pressure regulation.

A plot of yield against atmospheric pressure at constant temperature of 40°C and a time of three hours gave us the optimum pressure for carbonation.

This is presented in figure 4:10.

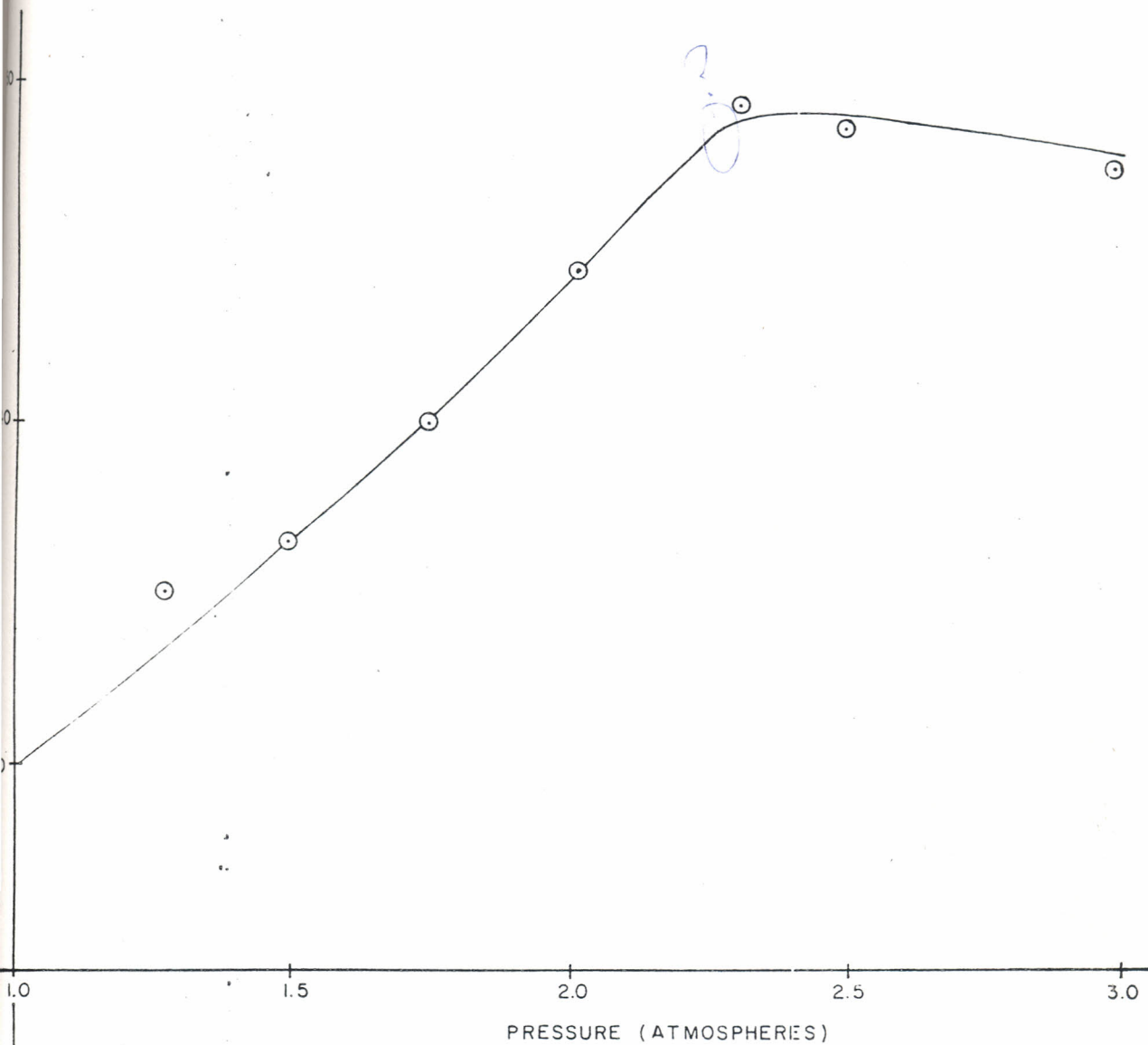


FIGURE 4.10 : YIELD OF SODIUM HYDROGEN CARBONATE AGAINST PRESSURE
AT TEMPERATURE 40°C AND TIME OF 3 HRS.

The pressure was regulated by the carbon dioxide gas being introduced into the vessel. The yield increased with increase in pressure upto a pressure of 2.5 atmospheres. Above 2.5 atm. increase in pressure did not alter the yield significantly.

Hence the optimum conditions for carbonation were found to be at temperature of 40°C, pressure of 2.5 atmospheres and an operation time of 3 hours. These conditions were used in the carbonation of Magadi soda ash.

4.5.2 MAGADI SODA ASH

Magadi soda ash was carbonated using all the pre-investigated conditions. A saturated solution of 50g/100g H₂O at a temperature of 40°C was prepared. This was put in the vessel placed in an air bath or water bath adjusted to temperature 40°C. Carbon dioxide gas or solid carbon dioxide was introduced in the vessel. The carbonation of Magadi soda ash gave a mean yield of 41% (S.D. 1.1%). The carbonation of light soda ash at these optimum conditions gave a yield of 45% (S.D. 1.1%).

Magadi soda ash therefore gave a lower yield than light soda ash. This could be attributed to the impurities and the big granules of magadi soda ash, that although they were ground as much as possible, it was still difficult to dissolve them.

The purity of sodium hydrogen carbonate formed from Magadi soda ash carbonation was found to be 90% (S.D. 1.6%),

with an impurity of water of 8.0%. The water impurity was propagated by failure of better methods of drying. Other impurities included 1.0% of sodium carbonate, 0.5% sodium fluoride and 0.5% of sodium chloride. Light soda ash gave a purity of 95% (S.D. 2.6%). There was 3.0% of water and 1.0% of sodium carbonate. Sodium fluoride and sodium chloride were not detected.

4.6 THERMODYNAMICS OF THE PROCESS

4.6.1 SOLUBILITY

The solubility of sodium carbonate was found to be higher than that of sodium hydrogen carbonate at low temperatures. The heats of solution of these salts support this. At 18°C the heat of solution of sodium carbonate is $-23.60 \text{ KJ mol}^{-1}$ while that of sodium hydrogen carbonate is $+18.0 \text{ KJ mol}^{-1}$. Thus, the dissolution of sodium carbonate is exothermic while that of sodium hydrogen carbonate is endothermic at 18°C. The heat of solution differences are expected to be largest at 40°C. Sodium carbonate solution was found to be at equilibrium with various solid phases at particular temperature. Table 4:9 presents various forms of sodium carbonate solid phases and their mode of crystallization at particular temperatures.

TABLE 4: 9 FORMS OF SODIUM CARBONATE

TEMPERATURE	SOLID PHASE	CRYSTALS
0°C	Na ₂ CO ₃	Flakes
20°C	Na ₂ CO ₃ .10H ₂ O	Monoclinic
37.5	Na ₂ CO ₃ .7H ₂ O	Orthorhombic
50	Na ₂ CO ₃ .H ₂ O	Rhombic

[26,27]

The heat of solution, ΔH_s^{298} , Gibbs free energy, ΔG_f° , heat of formation ΔH_f and entropy ΔS of the various forms of sodium carbonate crystals are presented in table 4:11.

TABLE 4:10 GIBBS FREE ENERGY

	ΔH_{298} (KJ mol ⁻¹)	ΔG_{298} (KJ mol ⁻¹)	ΔH_s (KJ mol ⁻¹)	ΔS (J mol ⁻¹ deg ⁻¹)
Na ₂ CO ₃ (s)	-1129.1 (-1134.0)	-1045.8 (-1050.6)	-23.6	136.8
Na ₂ CO ₃ .H ₂ O(s)	-1428.7 (-1433.9)	-1286.6 (-1291.3)	-9.4	-
Na ₂ CO ₃ .7H ₂ O(s)	-3192.7 (-3203.4)	-2715.0 (-2710.8)	-	(395.4)
Na ₂ CO ₃ .10H ₂ O(s)	-4075.8 (-4083.5)	-3428.6 (-3424.3)	67.7	(536.4)

() means calculated

[27]

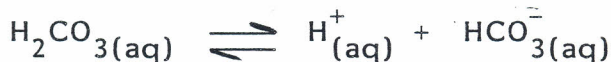
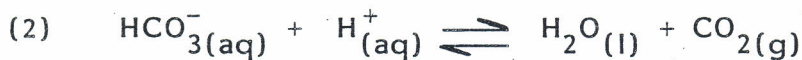
The heats of formation, ΔH_f , and Gibbs free energy, ΔG , increase with increase in water of crystallization of the solid phases. Heat of solution, ΔH_s , shifts from exothermic to endothermic with

increase of water of crystallization. This implies that it is difficult to dissolve sodium carbonate decahydrate as compared to anhydrous sodium carbonate. Nevertheless the largest solubility value is for sodium carbonate monohydrate of 50g/100g H₂O at 40°C.

From the equations



Sodium carbonate solution was found to be a stronger alkali compared to sodium hydrogen carbonate. The ionisation of sodium hydrogen carbonate follows two steps



Sodium hydrogen carbonate is referred to as an acidic salt. The salt solution was found to be in equilibrium with crystals containing no water of crystallisation. However there are sodium hydrogen carbonate dihydrate and sodium hydrogen carbonate trihydrate said to be in existence along side the anhydrous salt [26]. Likewise the heats of formation of all the three salts are given below in Table 4:12.

TABLE 4: 11 HEATS OF FORMATION FOR VARIOUS FORMS OF SODIUM HYDROGEN CARBONATE

FORM	$\Delta H^\circ, \text{KJ mol}^{-1}$
NaHCO_3	-947.7
$\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$	-1241.0
$\text{NaHCO}_3 \cdot 3\text{H}_2\text{O}$	-1523.8

[26,27]

The heats of formation ΔH_f° at standard temperature and pressure likewise increase with increase in water of crystallization.

4.6.2 CARBONATION

The carbonation reaction of the saturated solution of sodium carbonate is favoured at low temperatures.



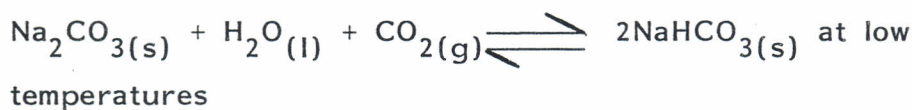
The Gibbs free energies for all compounds in the system are presented in Table 4:13.

TABLE 4:12 GIBBS FREE ENERGIES AT VARIOUS TEMPERATURES

TEMPERATURE	$\Delta G_f \text{ KJ mol}^{-1}$			
	$\text{Na}_2\text{CO}_{3(s)}$	$\text{H}_2\text{O}_{(l)}$	$\text{CO}_{2(g)}$	$\text{NaHCO}_{3(s)}$
20	-1048.5	-237.9	-394.2	-854.0
25	-1047.7	-237.2	-394.2	-853.1
30	-1045.7	-236.2	-394.2	-851.4
35	-1044.3	-235.4	-394.2	-850.1
40	-1042.9	-234.6	-394.2	-848.7
45	-1041.5	-233.8	-394.2	-847.4
50	-1040.1	-233.0	-394.3	-846.1

Free energies for all the compounds except carbon dioxide gas decrease exothermally with increase in temperature. Carbon dioxide gas exothermic free energy increase with increase in temperature. The calculated free energy for the system of carbonation at various temperature is presented in Table 4:14.

TABLE 4:13 GIBBS FREE ENERGY FOR THE SYSTEM



TEMPERATURE (°C)	ΔG_f (KJ mol ⁻¹)
20	-25.5
25	-24.7
30	-23.5
35	-22.4
40	-21.4
45	-20.4
50	-19.4

Likewise the exothermic Gibbs free energy decrease with increase in temperature. The trend was compared with that of one of the most soluble salt zinc chloride at low temperatures.

TABLE 4.14 GIBBS FREE ENERGY FOR ZnCl₂ SALT

TEMPERATURE (°C)	ΔG_f (KJ mol ⁻¹) ZnCl ₂
20	-370.0
25	-369.4
30	-368.5
35	-367.7
40	-366.9
45	-366.2
50	-365.4

[26]

The Gibbs free energy for zinc chloride also shows the same trend as that of the system.

From the Gibbs free energy, it can be concluded that the reaction, for the formation of sodium hydrogen carbonate is spontaneous. The shift of the equilibrium to the right was also improved by pressure. This was investigated in the stability studies of sodium hydrogen carbonate discussed earlier in this work.

4.7 SUMMARY

The volumetric method for analysis was found to be considerably accurate for this system. Concentrations of 10 ppm of both sodium carbonate and sodium hydrogen carbonate were easily determined through this analytical method. The mixed indicators used, methyl orange-indigo carmine and thymol blue-cresol red gave sharp colour change in 0.05-0.1 cm³ acid range using 0.1 M hydrochloric acid. However 0.01 M hydrochloric acid did not yield good results with this analytical method. The acid failed to give a sharp endpoint even with 0.1 v/v dilute indicators.

Study was done to incorporate the pH meter with the analysis method. The pH of 8.3 and 3.7 of the solution's endpoint were determined. The concentrations of various unknown alkaline solutions were determined more easily by attaining the 8.3 and 3.7 pH readings from the pH meter. Distinct colours of the mixed indicators at these pH readings were established. A characteristic yellow colour of thymol blue-cresol red indicator at pH 3.7. A characteristic colour of grey-magenta was established for methyl orange-indigo carmine indicator at pH 8.3. The colours and/or pH meter were used in the analysis.

Light soda ash and Magadi soda ash were analysed and used in the manufacture of sodium hydrogen carbonate. In the analysis it was found out that light soda ash contained no sodium fluoride. The magadi soda ash contained 0.9 ppm of sodium fluoride. Through the conversion this turned out to be 0.5 ppm. This was found and considered to be a trace amount.

The Magadi soda ash finds its markets in various countries for pharmaceutical and chemical use. This shows that the sodium

fluoride in it does not affect the end products as such.

The Magadi soda ash is quite cheap as compared to light soda ash. Twiga chemical industries, the sole distributor of Magadi soda ash, sold magadi soda ash at KSh. 3.15 and the light soda ash at KSh. 11.20 per kilogram. Thus light soda ash is four times as expensive as Magadi soda ash.

The solubility studies revealed that sodium hydrogen carbonate has a low solubility than sodium carbonate at low temperatures. From the figures 4.1 and 4.5 it is inferred that the solubility difference is greatest at the temperature 40°C when the solubility of sodium carbonate is largest. This means that the separation of the two salts by solubility differences will be easier. Hence the best temperature of carbonation of sodium carbonate. The solubility curve of sodium carbonate was found to increase sharply at low temperatures and reduced gradually at higher temperatures. The solubility curve of sodium hydrogen carbonate increased steadily and gradually at low temperatures.

Density plots against solubilities of both sodium salts were found to have a direct relationship.

$$\delta = KS + \delta_{H_2O}$$

K = solubility constant

δ_{H_2O} = density of water

δ = density of salt solution

S = solubility of the solution

The density of the solution depended on the solubility of the solution and the density of water. When no solid had been dissolved the density obtained was that of pure water. This corresponds to the y-intercept of the graphs.

In mutual solubility of the two sodium salts, it was found out that a greater amount of sodium carbonate dissolved in a

saturated solution of sodium hydrogen carbonate compared to the case where sodium hydrogen carbonate dissolved in a saturated solution of sodium carbonate.

At higher temperatures and vigorous stirring, sodium hydrogen carbonate solution lost some carbon dioxide to form sodium carbonate. As is the case, sodium carbonate has a higher solubility than sodium hydrogen carbonate. Hence in forming sodium carbonate in solution, room for dissolving more solid was created giving us unsaturated solution of both sodium hydrogen carbonate and sodium carbonate [27].

From the equation



If the reaction goes to the right, then two moles of sodium hydrogen carbonate are required to form one mole of sodium carbonate. This augments the above paragraphs explanation. This does not agree when sodium hydrogen carbonate is dissolved in a saturated solution of sodium carbonate.

Dry pure sodium hydrogen carbonate was found to be stable for a considerable length of time, three months. However better storage was achieved by putting sodium hydrogen carbonate in a closed system containing carbon dioxide. This reduced the shifting, of the above equation, to the right.

The carbonation of both light soda ash and magadi soda ash was proved to be effective beyond any reasonable doubt. A yield of 45% at a temperature of 40°C, 3 hours, and 2.5 atmospheric pressure was achieved with light soda ash and of 40% at the same

conditions was achieved for Magadi soda ash. Both solid and gas carbon dioxide was used with solid giving slightly better yields than the gas. The solid gave an improved yield of 1% with less time. The process was found to be simple and straight forward. The major constraint was to have a pressurizable vessel which would be heated easily. The grinding and dissolution may be done on a large scale.

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