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**INVESTIGATION OF SODIUM CARBONATE, SODIUM BICARBONATE AND
WATER SYSTEMS FOR SATURATED SOLAR PONDS**

Final Report

March 28, 1980

Work Performed Under Contract No. AC04-79CS12142

**InterTechnology/Solar Corporation
Warrenton, Virginia**

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U.S. Department of Energy

Solar Energy

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Final Report
28 March 1980

Prepared for
U.S. Department of Energy
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ABSTRACT

The overall objective of this study was to gather relevant data primarily from the published literature to investigate the technical feasibility of using a Na_2CO_3 - NaHCO_3 mixture for a saturated solar pond.

This objective was accomplished by a literature search and review of existing chemical information and by performing simple chemistry experiments in the laboratory. Information on density, solubility, phase diagram, equilibrium compositions, reaction rate constant, equilibrium constant, diffusion coefficient, vapor pressure and potentially useful additives is compiled in this report.

It is concluded that even though both the saturation density and solubility increase with temperature for trona, it is not chemically stable either at room temperature or higher temperatures (80°C). Therefore, as is, trona is not suitable for use in a saturated solar pond. From the literature it has been found that sugar and gum can retard the decomposition of bicarbonate to carbonate in the mixture. Nevertheless, trona is a very attractive solute for an unsaturated solar pond. A laboratory unsaturated pond with a stable density gradient has worked without any problems for about two months at InterTechnology/Solar Corporation.

Equilibrium compositions of mixtures of sodium carbonate and sodium bicarbonate with initial mole ratios of 4:1, 6:1 and 8:1 have been found to lie between 5:1 and 6:1. Mixtures having initial mole ratios of 2:1 and 3:1 reached a value of about 3.5:1 in 6 months, and this ratio was still increasing. The diffusion coefficient of trona from saturated solution in distilled water was experimentally found to be equal to $0.86 \times 10^{-5} \text{ cm}^2/\text{sec}$ which is about half of that for NaCl under identical conditions. Thus an unsaturated trona solar pond will need about half the amount of salt makeup as a sodium chloride pond with the same concentration gradient. A trona solution saturated at 60°C when kept at

60-70°C was found to have a carbonate to bicarbonate ratio equal to 3.8 in 95 days.

Based on limited experimental data and published information, it appears that a saturated solar pond open to the atmosphere will work with a sodium carbonate-sodium bicarbonate mixture in the mole ratio between 4 to 6. Further work is required to test a laboratory pond with this mixture with the mole ratio between 4 and 6.

Recommendations for future work in this area are outlined particularly for better understanding of the system from a chemical stability viewpoint. More research in the area of suitable additives for retarding decomposition of sodium bicarbonate to carbonate is also needed. A regional applicability study to investigate the potential, economics and the end use of this mixture in solar pond systems in the U.S. should be pursued.

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Gurmukh D. Mehta

1.0 STATEMENT OF THE PROBLEM

This report documents the technical results achieved under DOE Contract DE-AC04-79CS12142 monitored by Los Alamos Scientific Laboratory during the period 1 October 1979 through 31 March 1980. The bulk of the technical effort was devoted to the evaluation of the system sodium carbonate-sodium bicarbonate-water for potential use in saturated solar ponds.

The scope of work of this contract was divided into the following four tasks:

Task 1: Literature Search and Review of Existing Chemical Information

Under this task literature was reviewed to determine existing data on the solubility, reaction constants, density, composition of saturated solutions in equilibrium with the atmosphere, vapor pressure, chemical diffusion, and potentially useful additives to the chemical system sodium carbonate-bicarbonate-water.

Task 2: Laboratory Experiments

Under this task laboratory experiments were done to determine physical and chemical properties such as the equilibrium concentrations, reaction rate constants and diffusion constant for the system under study as these data were relevant to the solar pond operation and were not available in the literature.

Task 3: Theoretical Analysis

Under this task an effort was made to understand the compositions of saturated solutions in equilibrium with the atmosphere at room temperature and at temperatures near 60°C.

Task 4: Integration of Information

Under this task the information developed in Tasks 1, 2 and 3 was integrated into this final report.

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2.0 INTRODUCTION

A solar pond is basically a shallow, artificial black-bottom pond or lake in which the incident solar radiation is converted into a local temperature rise in the water near the bottom. It is crucial for the success of such a system that there is a high temperature at the bottom and simultaneously a low temperature at the top of the pond to minimize excessive energy losses through evaporation, conduction and radiation from the top surface.

The above thermal objectives cannot be achieved by using a pond containing water alone. The higher temperature at the bottom of the pond decreases its density relative to that at the surface, thus causing convection currents which quickly equalize the water temperature. The thermal convection currents in the pond can be suppressed by forming stable, vertical density gradients through the addition of salt.

Since the first systematic study by Tabor (1) in 1959, several artificial solar ponds have been built and tested in Israel and, more recently, in the United States. The results of a number of recent studies show that a solar pond system is more economical for space heating and industrial process heating than conventional solar collector systems. Moreover, because of lower collector costs and "built-in" storage, solar pond systems can also be used for power generation.

The chief problem with the conventional, unsaturated, salt-stratified pond as presently conceived is that of establishing and, even more important, maintaining the salt concentration gradient so necessary for pond stability. Unfortunately the existence of a salt concentration gradient causes salt diffusion, thus tending continuously to destroy the gradient. Because of the diffusion of salt from the bottom to the top of the pond, it is necessary to wash the top layer of the pond with fresh water and to inject salt at the bottom of the pond continuously.

The problem of pond mixing due to salt diffusion can be eliminated by utilizing a pond saturated with a solute whose solubility increases with temperature. In such a pond the salt concentration gradient would be self-generated and self-maintained depending upon the local temperature. Thus, for saturated salt ponds the need for removing salt from the pond surface and injecting salt at the bottom of the pond is eliminated. Compared to an unsaturated solar pond, a saturated salt pond, in principle, would be simpler in construction and operation. However, no such field pond has been built so far because of the apparent lack of a temperature-sensitive solute that is cheap, stable, nontoxic, transparent, and available in large quantities, and has an average solubility which, over the pond temperature range of 20 to 100°C, is not too high.

There are a number of solutes (for example, KNO_3 , CaCl_2 , NH_4NO_3) the solubility of which in water increase with temperature as shown in Figure 1. However, the solubility and cost of these solutes are too high to be economical.

In an internally funded study, InterTechnology/Solar Corporation has explored the feasibility of a number of solutes, not previously studied, which can be used for saturated solar ponds, including K_2SO_4 , NaHCO_3 , KClO_4 , borax, and trona (sodium sesquicarbonate $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). Of all the different solutes investigated, trona and other combinations of Na_2CO_3 and NaHCO_3 appear to be the most promising. Sodium bicarbonate by itself is stable up to only 60°C. At higher temperatures, it decomposes into sodium carbonate and CO_2 . Although sodium carbonate is stable over the entire temperature range, its solubility is insensitive to temperature. In contrast, according to the published literature (2), the solubility of trona increases with temperature, and trona is stable over the desired temperature range. The variation of the solubility of NaHCO_3 and trona with temperature is plotted in Figure 1 for comparison purposes. Thus, trona can be used in a saturated solar pond up to

100°C, and its average solubility is one order of magnitude smaller than that of other solutes previously considered.

Furthermore, trona is naturally available in relatively pure form and in large quantities from several sources. An estimated 17 billion tons of quite pure trona is available at Green River, Wyoming (3). This amount alone would be sufficient for about 500 solar pond systems of 1000 MW_e capacity each. Moreover, since this material is a natural product requiring only mining and crushing, it should be cheap and very economical to use as compared to other solutes. It is expected that natural trona, which is more than 95% pure, could be available in the southwest United States at a cost as low as 2.5¢/kg.

Trona is primarily used to manufacture soda ash (Na₂CO₃), which itself is very cheap, thereby making the mixtures of Na₂CO₃ and NaHCO₃ very attractive candidates. The main objective of this study was to investigate the technical feasibility of using Na₂CO₃-NaHCO₃ systems for saturated solar pond applications.

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3.0 OBJECTIVES

The overall goal of this study was to determine all the characteristics of the system sodium carbonate-sodium carbonate-water which are useful for solar pond application, including the chemical stability of the mixture from solution freezing point to 100°C. The goals were addressed by:

1. Performing a literature search and review of existing chemical information on the system under consideration. This information included solubility, reaction constants, density, composition of saturated solutions in equilibrium with the atmosphere, vapor pressure, chemical diffusion and any other physical or chemical properties relevant to solar pond application. Information was also gathered on potentially useful additives to the system which can retard the decomposition of sodium bicarbonate to sodium carbonate.
2. Performing laboratory experiments to determine those properties which could not be found in the literature but are relevant to solar pond application.

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4.0 LITERATURE SEARCH

The information on various properties and characteristics of the system (sodium carbonate-sodium bicarbonate-water) obtained from the literature is listed in the following subsections:

4.1 Solubility

Trona is a double salt stable in contact with saturated solutions between 21.26°C and 195±5°C (4,5). At 150°C and lower temperatures, trona is incongruently* soluble; at about 160°C it is congruently soluble, and at 170°C it is again incongruently soluble (4, 5, 6). Freeth (7) reports that sodium sesquicarbonate (trona) is not stable in contact with solutions containing the same molar proportion of Na_2CO_3 and NaHCO_3 as itself. As a consequence, any attempt to produce a saturated solution from trona and water above 20°C results in the formation of NaHCO_3 before the three-phase area NaHCO_3 -sesquicarbonate-solution is reached. Eugster (6) reported this behavior as incongruent solubility. All systems studied in References 4 to 7 were closed systems.

4.2 Density

Hill and Bacon (4) reported the solution densities given in Table 1 for sodium carbonate-sodium bicarbonate-water systems in closed containers and for 24.87°C, 30°C, and 50°C isotherms.

These data suggest, for example, that the progressive removal of water from a solution at 24.87°C with a solution density of 1.216, containing 17.85% Na_2CO_3 and 4% NaHCO_3 by weight, will result in the precipitation of both NaHCO_3 and trona salts in closed systems. However, for similar

* Incongruent solubility means that a brine formed by the dissolution of dilute trona solution (equal molar proportions of carbonate and bicarbonate) will precipitate bicarbonate (nahcolite) upon removal of water. See Figures 2 and 3.

conditions and solution densities of 1.225, 1.228, 1.240 and their corresponding solution weight percentages of Na_2CO_3 and NaHCO_3 , trona alone is precipitated upon progressive removal of water. This type of information is used to generate diagrams such as Figures 2 and 3. It can be seen that these results generally correspond to the diagrams shown in Figures 2 and 3; as the weight percentage of NaHCO_3 in solution decreases (moving to the left on the bottom axis of Figure 3 from nahcolite to natron), the solid phase changes from NaHCO_3 to trona to the hydrates of Na_2CO_3 .

4.3 Vapor Pressure

Mellor (8) stated that trona at 100°C gives an approximate constant vapor pressure of 496 mm Hg until a large part of the water is removed (e.g., moving along line 1 in Figure 3 to point a). At this point, water has been removed but little CO_2 has been lost. As CO_2 is removed (e.g., moving from point a to c in Figure 3), the vapor pressure drops to 182 mm Hg where it remains constant until all of the salt is converted into anhydrous Na_2CO_3 (the lower left-hand corner of Figure 3). It is not clear from the report whether these results were obtained for open or closed systems.

4.4 Potentially Useful Additives

Mellor (8) reports that V. Urbain (9) found the dissociation of NaHCO_3 to be retarded when sugar or gum was added to the solution.

4.5 Equilibrium

McCoy (10) presented an empirical formula for predicting the equilibrium composition of the system composed of sodium carbonate, sodium bicarbonate, carbon dioxide, and water at constant temperature. The formula was developed experimentally, by determination of the composition of the liquid and vapor phases in equilibrium with one another, at constant temperature (25°C), for various proportions of constituents. The formula is:

$$\frac{2 X^2 C}{SP(1-X)} = K' \quad (1)$$

where X is the fraction of sodium in the form of bicarbonate

1-X is the fraction of sodium in the form of carbonate

C is the concentration of sodium in gram-atoms per liter

S is the solubility coefficient of carbon dioxide in water at the equilibrium temperature, gm-moles/liter

P is the partial pressure of the carbon dioxide, atm

K' is the equilibrium constant and is equal to 53×10^2 (1/atm) for dilute solutions

Harte et al. (11) performed experiments to determine the equilibrium relationship between temperature, partial pressure of carbon dioxide in the gas phase, and chemical composition of the liquid for a range of conditions. The results of these experiments and those of McCoy (10) were correlated in an empirical equation, representing the equilibrium relationship between temperature, partial pressure of carbon dioxide in the gas, and chemical composition of the solution.

Experimental work by McCoy (10) and by Sieverts and Fritzche (12) indicated that the value of K' in Equation (1) is independent of P and X, but that it varies with temperature and with total sodium concentration. The practical significance of these experimental findings is: (i) at a particular temperature and for a particular total sodium concentration, a single value of K' will permit the calculation of the corresponding equilibrium values, X and P; (ii) every new set of conditions, in which either temperature or total sodium concentration takes on a new value, requires a new value of K'. Equation (1) would furnish all the desired information concerning equilibrium if reliable values of K' for a desired range of temperature and sodium concentrations were available.

The experimental values of K' determined by Harte et al. (11), along with those previously available in the literature, provide a range of sodium concentrations between 0.5 and 2.0 normal at temperatures from 20 to 70°C.

The experimental results along with the previous results obtained by McCoy (10) were correlated by means of an empirical equation:

$$K' = 20 (185 - T)C^{-0.29} \quad (2)$$

where T is the temperature in °C.

Combining Equations (1) and (2) gives:

$$\frac{X^2 C^{1.29}}{SP(1-X)(185-T)} = 10 \quad (3)$$

Equation (3) can be used to calculate equilibrium relationships for any values of C and T within the range of the experimental work (20 to 70°C, 0.5 to 2.0 gram atoms per liter or normal in sodium, 20 to 70°C).

Using Equation (3), we calculated the equilibrium concentrations of solutions having initial concentrations of sodium carbonate-sodium bicarbonate equivalent to saturated trona, and sodium carbonate-sodium bicarbonate in the ratio of 3:2 at 20°C and 80°C. The results are summarized in Table 2.

Normalities (column 2, Table 2) were calculated from the solubility curve for trona solutions given in Figure 4 and the solubility curve for Na_2CO_3 - NaHCO_3 solutions in the ratio of 3:2 in Figure 5 of this report.

Equation (3) can also be used to calculate the concentration of CO_2 in air needed for solutions of trona (1:1) or any other Na_2CO_3 - NaHCO_3 mixture to be stable at various temperatures. Substituting the appropriate values for trona into Equation (3) produces figures of 0.0088 atm

(approximately 30 times the normal CO_2 concentration in air, 0.0003 atm) and 0.1044 atm (approximately 350 times the concentration of CO_2 in air) of CO_2 at temperatures of 20° and 80°C , respectively.

The equilibrium molecular ratios shown in Table 2 are supported by data reported by Bradley and Eugster (13). Figure 6, taken from their report, shows that extrapolation to the CO_2 content of air yields a bicarbonate quotient, defined as
$$\frac{\text{HCO}_3 \text{ (gm)}}{\text{HCO}_3 \text{ (gm)} + \text{CO}_3 \text{ (gm)}} ,$$
 of about 0.15, which is equivalent to a $\text{Na}_2\text{CO}_3:\text{NaHCO}_3$ ratio of 5.7:1.

The information obtained by using the empirical Equation (3) to calculate the equilibrium composition does not cover the sodium normality range corresponding to saturated trona solutions in the desired temperature range. This information is a necessary requirement in predicting the stability and self-maintenance characteristics of a trona saturated solar pond.

An attempt was made in the laboratory to determine the equilibrium composition of a saturated trona solution at room temperature and at about 60°C , but because of time limitations, equilibrium was not reached. Concentration data as a function of time are given in the experimental section of this report.

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5.0 EXPERIMENTAL WORK

The data on equilibrium compositions found in the literature were limited in sodium normality to the range from 0.5 to 2.0. However, for saturated solutions of 1:1 and 3:2 sodium carbonate-sodium bicarbonate mixtures in a saturated solar pond operating between 20°C and 80°C, the sodium normality is higher than 2.0. Also, no data on kinetic rate constants and on the diffusion coefficient could be found in the literature. Laboratory experiments were performed for determining the equilibrium compositions of saturated trona solutions at 20°C and 60°C, diffusion coefficient of saturated trona solution in water at 25°C, and kinetic rate constant at room temperature. These experiments are discussed in the following subsections.

5.1 Density

Densities of some saturated solutions as a function of temperature are shown in Figures 4 and 5, respectively. As the density of saturated solutions for both mixtures (trona and 3:2) increases with temperature, both are suitable for saturated solar pond, provided they are chemically stable in the pond.

5.2 Titration Technique

There are two titration techniques available for analyzing sodium carbonate and sodium bicarbonate in solution. Both of these methods are discussed in detail in the Appendix. The method which utilizes BaCl_2 and NaOH was used in all the experiments presented here.

5.3 Equilibrium Composition

As the information on equilibrium compositions of saturated solutions of mixtures of sodium carbonate-sodium bicarbonate in various composition ranges were not available in the literature, experiments were conducted to generate some of this information in the laboratory.

Three experiments were established to study the changes in the composition of mixtures of sodium carbonate and sodium bicarbonate in various mole ratios. The first experiment was designed to study the composition of solutions of various mixtures as a function of time. The other two experiments were designed to study the equilibrium compositions of saturated trona solutions at 20°C and 60°C. These three experiments are discussed in detail in the following paragraphs:

5.3.1 Containers Test

In this test laboratory test solutions in separate plastic containers (500 cc) were made from sodium carbonate and sodium bicarbonate in the mole ratios of 1:1, 2:1, 3:1, 4:1, 6:1 and 8:1 of sodium carbonate to sodium bicarbonate. All solutions were 15% anhydrous solute by weight. In the case of 1:1, 2:1 and 3:1 mixture solutions, two containers for each mixture were made. One set of containers was left open to the atmosphere while the other set was covered at the top but not sealed. The 4:1, 6:1 and 8:1 mixture solutions were left open to the atmosphere. All of these solutions were analyzed periodically by titration for sodium carbonate and sodium bicarbonate to determine the chemically stable or equilibrium ratio. This test was continued for about 6 months. The results of this test are given in Table 3 and shown in Figures 7 and 8.

5.3.2 Equilibrium Composition of Saturated Trona Solution at 20°C

In this test a 5-gallon saturated trona solution at 20°C (15% anhydrous trona by weight) was made in a 10-gallon polypropylene tank (1.5' x 1' x 1'). Air was continuously bubbled through this solution in order to provide a good surface contact between atmospheric air and the solution so that the equilibrium could be reached as quickly as possible. A constant liquid level in the tank was maintained by means of a water bird bath. This test was run for 3 months. During the test solution samples were analyzed periodically to determine whether equilibrium was

reached or not. Results of these analyses are given in Table 4. Equilibrium was not reached during the 3-month period, and because time was limited this experiment was discontinued after 3 months.

5.3.3 Equilibrium Composition of Saturated Trona Solution at 60°C

In this test saturated trona solution was made in a 5-gallon polypropylene tank at 60°C. The tank was equipped with a copper-coil heat exchanger. By circulating hot water through this heat exchanger, the solution was kept at 60°C. A birdbath was provided to compensate for water losses due to evaporation, thereby maintaining a constant solution level in the tank. A Hake Model E52 heater and pump unit along with an external water bath connected to the copper-coil heat exchanger in the tank was used as the heat source for maintaining the temperature of the solution. This heating unit has a built-in thermal regulator and ten heat settings. The temperature of the bath could be controlled within $\pm 1^\circ\text{C}$ by means of a thermal regulator. Since the evaporation rate at 60°C is quite high, an arrangement to pump water every four hours into the tank to make up for water evaporation was also provided.

Concentrations of the solutions were analyzed by titration from time to time. Results of this test are given in Table 5. This test was carried out for 95 days. Results shown in Table 5 indicate that equilibrium was not attained even in 95 days. Time and funding limitations did not permit the determination of actual equilibrium conditions.

5.4 Kinetic Rate Constants

A scheme for determining forward and backward reaction rate constants for the overall reaction involved in the decomposition of sodium bicarbonate to sodium carbonate in a saturated trona solution at room temperature is given here. A laboratory experiment was also performed for determining trona composition as a function of time. Since the equilibrium constant could not be determined, the numerical values of forward and backward reaction rate constants are not calculated in this report.

The overall reaction in the decomposition process is:

As no information on the reaction rate mechanism was available from the literature, a simple reaction rate model according to the overall reaction was assumed. According to this model, the rate equation can be written as:

$$\frac{-d [\text{NaHCO}_3]}{dt} = k_F [\text{NaHCO}_3]^2 - k_R [\text{Na}_2\text{CO}_3][\text{CO}_2][\text{H}_2\text{O}] \quad (5)$$

At equilibrium, the forward reaction rate is equal to the backward reaction rate and hence

$$K = \frac{k_F}{k_R} = \frac{[\text{Na}_2\text{CO}_3]_{eq} [\text{CO}_2]_{eq} [\text{H}_2\text{O}]_{eq}}{[\text{NaHCO}_3]_{eq}^2} \quad (6)$$

where

$[\text{NaHCO}_3]$ = concentration of sodium bicarbonate at any time t
at room temperature, gm mole/liter

$[\text{NaHCO}_3]_{eq}$ = equilibrium concentration of sodium bicarbonate at
room temperature, gm mole/liter

$[\text{Na}_2\text{CO}_3]$ = concentration of sodium carbonate at any time t
at room temperature, gm mole/liter

$[\text{Na}_2\text{CO}_3]_{eq}$ = equilibrium concentration of sodium carbonate at
room temperature, gm mole/liter

$[CO_2]$	=	concentration of carbon dioxide in solution at any time t at room temperature, gm mole/liter
$[CO_2]_s$	=	saturation concentration of carbon dioxide at room temperature, gm mole/liter
$[CO_2]_{eq}$	=	equilibrium concentration of carbon dioxide in solution at room temperature gm mole/liter
$[H_2O]$	=	concentration of water at any time t at room temperature, gm mole/liter
$[H_2O]_{eq}$	=	equilibrium concentration of water at room temperature, gm mole/liter
k_F	=	forward reaction rate constant, liter/(gm mole)(hr)
k_R	=	backward reaction rate constant, $\frac{(\text{liter})^2}{(\text{gm mole})^2(\text{hr})}$
K	=	equilibrium constant = k_F/k_R = gm mole/liter

Since

$$[CO_2]_{eq} = [CO_2]_s$$

We can rewrite Equation (6) as:

$$K = \frac{k_F}{k_R} = \frac{[Na_2CO_3]_{eq} [CO_2]_s [H_2O]_{eq}}{[NaHCO_3]_{eq}^2} \quad (7)$$

Equations (5) and (7) when solved will give the values of k_F and k_R .

Let

$[\text{Na}_2\text{CO}_3]_0$ = initial concentration of sodium carbonate,
gm mole/liter,

$[\text{NaHCO}_3]_0$ = initial concentration of sodium bicarbonate,
gm mole/liter, and

$[\text{H}_2\text{O}]_0$ = initial concentration of water, gm mole/liter

Further, assuming that the decomposition of NaHCO_3 to Na_2CO_3 in the solution is so fast that at the time the first data are taken, the solution is already saturated with carbon dioxide,* i.e.,

$$[\text{CO}_2] = [\text{CO}_2]_s.$$

$[\text{Na}_2\text{CO}_3]$ and $[\text{H}_2\text{O}]$ can now be expressed in terms of initial concentrations and the concentration $[\text{NaHCO}_3]$ as follows:

$$[\text{Na}_2\text{CO}_3] = [\text{Na}_2\text{CO}_3]_0 + \frac{1}{2} [\text{NaHCO}_3]_0 - \frac{1}{2} [\text{NaHCO}_3]$$

$$[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_0 + \frac{1}{2} [\text{NaHCO}_3]_0 - \frac{1}{2} [\text{NaHCO}_3]$$

Equation (5) can now be rewritten in terms of initial concentrations and the concentration of sodium bicarbonate at any time t as follows:

$$\frac{-d [\text{NaHCO}_3]}{dt} = k_F [\text{NaHCO}_3]^2 - k_R ([\text{Na}_2\text{CO}_3]_0 + \frac{1}{2} [\text{NaHCO}_3]_0 - \frac{1}{2} [\text{NaHCO}_3]) ([\text{H}_2\text{O}]_0 + \frac{1}{2} [\text{NaHCO}_3]_0 - \frac{1}{2} [\text{NaHCO}_3]) [\text{CO}_2]_s$$

or

* This has been observed in our laboratory.

$$\begin{aligned} \frac{-d [\text{NaHCO}_3]}{dt} = & \left(k_F - \frac{k_R}{4} [\text{CO}_2]_S \right) [\text{NaHCO}_3]^2 + \frac{k_R}{2} [\text{CO}_2]_S ([\text{Na}_2\text{CO}_3]_0 + [\text{H}_2\text{O}]_0 \\ & + [\text{NaHCO}_3]_0) [\text{NaHCO}_3] - k_R [\text{CO}_2]_S ([\text{Na}_2\text{CO}_3]_0 + \frac{1}{2} [\text{NaHCO}_3]_0) ([\text{H}_2\text{O}]_0 + \\ & \frac{1}{2} [\text{NaHCO}_3]_0) \end{aligned} \quad (8)$$

Let

$$a = - [\text{CO}_2]_S ([\text{Na}_2\text{CO}_3]_0 + \frac{1}{2} [\text{NaHCO}_3]_0) ([\text{H}_2\text{O}]_0 + \frac{1}{2} [\text{NaHCO}_3]_0), \quad (9a)$$

$$b = \frac{1}{2} [\text{CO}_2]_S ([\text{Na}_2\text{CO}_3]_0 + [\text{H}_2\text{O}]_0 + [\text{NaHCO}_3]_0), \text{ and} \quad (9b)$$

$$c = \frac{k_F}{k_R} - \frac{1}{4} [\text{CO}_2]_S = K - \frac{1}{4} [\text{CO}_2]_S \quad (9c)$$

Equation (8) can now be expressed in terms of a, b and c as:

$$\frac{-d [\text{NaHCO}_3]}{dt} = k_R (a + b [\text{NaHCO}_3] + c [\text{NaHCO}_3]^2) \quad (10)$$

On integration we get:

$$k_R t + \frac{1}{\sqrt{-q}} \ln \frac{2c [\text{NaHCO}_3] + b - \sqrt{-q}}{2c (\text{NaHCO}_3)_0 + b + \sqrt{-q}} + \text{Constant} = 0 \quad (11)$$

where $q = 4ac - b^2$ and $b^2 > 4ac$

At $t = 0$

$$[\text{NaHCO}_3] = [\text{NaHCO}_3]_0$$

and hence

$$\text{Constant} = - \frac{1}{\sqrt{-q}} \ln \frac{2c [\text{NaHCO}_3]_0 + b - \sqrt{-q}}{2c [\text{NaHCO}_3]_0 + b + \sqrt{-q}}$$

On substituting the value of the integration constant in Equation (11), we get:

$$\begin{aligned}
t = & - \frac{1}{k_R \sqrt{-q}} \ln \frac{2c [\text{NaHCO}_3] + b - \sqrt{-q}}{2c [\text{NaHCO}_3] + b + \sqrt{-q}} \\
& + \frac{1}{k_R \sqrt{-q}} \ln \frac{2c [\text{NaHCO}_3]_0 + b - \sqrt{-q}}{2c [\text{NaHCO}_3]_0 + b + \sqrt{-q}}
\end{aligned} \tag{12}$$

Now if we plot t against $\ln \frac{2c [\text{NaHCO}_3] + b - \sqrt{-q}}{2c [\text{NaHCO}_3] + b + \sqrt{-q}}$,

a straight line will result and its slope will be equal to $-\frac{1}{k_R \sqrt{-q}}$

which will enable us to calculate k_R and finally k_F from the equilibrium constant. The experimental procedure and the method of determining the rate constants are discussed in the next subsection.

5.4.1 Equilibrium Constant

The determination of the equilibrium composition is necessary for determining equilibrium constant and the reaction rate constants. As described in Section 5.3.2, an attempt was made in the laboratory to determine the equilibrium composition for a trona solution saturated at 20°C. As equilibrium was not attained in 3 months, it was not possible to calculate the value of the equilibrium constant by use of Equation (7).

5.4.2 Experimental Procedure and Results

Fifteen percent trona solution was made in a 5-gallon polypropylene tank from sodium monohydrate and sodium bicarbonate by mixing them in equimolar quantities. This solution was analyzed for sodium carbonate and sodium bicarbonate contents as a function of time. Results are given in Table 6. Since the value of the equilibrium constant was not determined, it was not possible to calculate the numerical values of forward and backward reaction rate constants by the scheme discussed in section 5.4. However, it would be possible to calculate the values of reaction rate constants from our data by employing another scheme given in section 5.4.3.

5.4.3 Method of Determining Reaction Rate Constants by Integration of Rate Equations and Numerical Analysis

Ideally, in the analysis of the kinetics of a simple chemical reaction, the basic rate equation would be integrated analytically to obtain a simple integral relationship of concentration as a function of time. This integral relationship would be used to calculate concentrations as a function of time for comparison with the data. The best fit with the data would be obtained to derive the best values for the kinetic rate parameters--the rate constants (pre-exponential factor and activation energy) and reaction orders.

If the integral relationship is simple enough, it perhaps can be manipulated to be plotted as a straight line for comparison with data. The "least squares" line would be calculated, and the best values of the rate parameters would be obtained from the intercept and slope.

However, in the analysis of even only a moderately complex chemical reaction, it frequently is not possible to obtain an analytical integral relationship from the basic rate equation for comparison with the data. It is then necessary to integrate the rate equation numerically with assumed values for the rate parameters to obtain predicted values of the concentrations for comparison with the data. The objective in fitting the data with the model is to find the values of the rate parameters which result in the "best" fit, the best fit being defined as the smallest sum of squares of the deviations between predicted values of concentrations and the data. This procedure involves a great deal of calculation, but can be done easily enough with an appropriate computer program.

In the analysis of the reactions in the carbonate-bicarbonate system, integrating the rate equation results in a relationship which cannot be used easily with the manual method of plotting and calculating the best squares line to obtain the best values for the rate parameters, even when first orders on the concentrations are assumed. Thus, ideally the

more powerful model/data fitting procedure, called "nonlinear estimation," should be used. With sufficient data, all rate parameters and even best values for reaction orders can be obtained simultaneously with the nonlinear estimation method.

ITC/Solar has a general-purpose nonlinear estimation program which can be used, with a minimum of programming (it would be necessary to program the specific rate expression), to analyze the carbonate-bicarbonate reaction data. All of the data could be used in the analysis--at least those data which appear to be compatible--to obtain values for the reaction rate constants and reaction orders, thus avoiding the use of a possibly spurious value of the equilibrium constant and assumed reaction orders.

This procedure is as follows:

1. Evaluate all of the kinetic data to determine which data can be used in an overall kinetic analysis (i.e., data all at the same temperature and which are representative of the same reactions).
2. Develop more general reaction rate expressions allowing for variable reaction orders.
3. Program the necessary subroutine for the nonlinear estimation program.
4. Run the program with the objective of finding the best fit of the model with the data which results in the best values of the reaction rate constants (forward and back reactions) and reaction orders on the concentrations in the rate expressions, the best fit being defined as giving the lowest sum of the squares of the deviations between predicted values of the concentrations and the data.

This more powerful model/data fitting procedure was not used because of limitations on the scope of the work.

5.5 Diffusion

The diffusion coefficient of trona at saturated concentration and 25°C in water was determined in the laboratory. The method used is a relative method and is described below. This method is both rapid and inexpensive and was first used by Schulze (14) and was later used by Wall et al. (15), who tested it with the diffusion of electrolyte in aqueous solution and for investigation of the diffusion of polymer molecules.

5.5.1 Diffusion Model¹⁶

This method consists of placing a porous, unglazed porcelain disk (frit) filled with the desired solution in a large bath of pure solvent or a solution of different concentration. The frit is suspended in the bath by a wire from one arm of an analytical balance which has been modified for this purpose (Tromner Balance), and the progress of diffusion is followed by recording the apparent weight of the frit with time. Consider the diffusion out of a homogenous cylindrical disk with plane parallel faces. The faces are large and the disk is thick, the problem can be simplified to one dimensional diffusion and Fick's law can be written as:

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial(D \frac{\partial C(x,t)}{\partial x})}{\partial x} \quad (13)$$

Where $C(t)$ is the concentration at the time t and at a distance x from the center of the disk along the normal to the faces. For the porous disk used here, Equation (13) will hold if an effective cross-sectional area A and an effective thickness $2L$ are defined so that the integral over these dimensions of $C(x,t)$ equals $Q(t)$, the amount of solute contained in the frit at time t . Clearly, these effective dimensions will

be less than the actual external dimensions of the disk, since the volume of solution held by the frit is less than the volume of the disk.

If the diffusion constant is assumed to be independent of concentration, or understood to be an average integral diffusion constant over the concentration range involved, Equation (13) can be readily solved. In terms of $Q(t)$, the result is¹¹

$$Q(t) = A \int_{-L}^L [C(x,t) - C_0] dx$$

$$= 2 LA(C_1 - C_0) \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-Dt(2n+1)^2\pi^2}{4L^2} \right] \quad (14)$$

where C_1 is the initial concentration in the frit at time $t = 0$ and C_0 is the concentration in the bath, which is assumed to be constant. If D is a function of concentration, the proper solution of equation (13) is much more difficult. In Equation (14), except for a short initial time period, the sum will be dominated by the first term ($n = 0$). For times sufficiently long that $t > 0.2 (4L^2/\pi^2 D)$, $Q(t)$ can simply be written as

$$Q(t) = 2LA (C_1 - C_0) \frac{8}{\pi^2} \exp \left(- \frac{D\pi^2 t}{4L^2} \right) \quad (15)$$

Let us define a quantity W_t as

$$W_t = W(t) - W(\infty) \quad (16)$$

where $W(t)$ is the apparent weight of the frit suspended in the bath at time t and $W(\infty)$ is the apparent weight after equilibrium has been reached. Clearly W_t is given by:

$$W_t = A \int_{-L}^L [d(x,t) - d_0] dx \quad (17)$$

where $d(x,t)$ is the density of the solution at point x and time t , and d_0 is the density of the liquid in the bath. If the density of the

solution as a function of concentration can be represented by a linear function $d(C) = d(o) + kC$, where $d(o)$ is the solvent density, we get

$$W_t = Ak \int_{-L}^L [C(x,t) - C_o] dx = kQ(t) \quad (18)$$

on substituting Equation (18) into Equation (15) and rearranging to a more convenient form, we get

$$\log W_t = - \frac{D\pi^2 t}{2.303(4L^2)} + \log [2LAk (C_1 - C_o) \frac{8}{\pi^2}] \quad (19)$$

Thus a plot of $\log W_t$ versus t will give a straight line of slope $(-\alpha D)$, where $\alpha = \frac{\pi^2}{2.303(4L^2)}$

is an "apparatus constant" characteristic of the frit used. A calibration of the frit with a solution of known diffusion properties will be required for evaluating the constant α . It should be noted that for short times (at the beginning of the diffusion) the points should lie above the straight line determined by the $\log W_t$ versus t points for longer times.

5.5.2 Experimental Procedure

The experimental setup consisted of an analytical balance (Tromner balance) mounted above a 25°C thermostat bath. The balance had a hole in the base on the right side, and thus the disk could be suspended by a fine wire from the right side of the balance into the solvent bath which was mounted in the thermostat. The solvent bath vessel consisted of a 2 liter beaker which had a sufficiently wide mouth to permit introduction of the porous disk and was mounted in the thermostat by clamping.

The edge of the porous disk might be sealed with a cement or resin to prevent radial diffusion, although this was not done as it is not

necessary to achieve good results. A small hole was drilled through the porous disk near the edge to permit attaching a fine wire.

Selas unglazed, microporous filter plate; 7.5 cm in diameter, 0.4 cm thick, grade 10 porosity was used as the porous plate. It had an external geometric volume of about 29 cc and dry weight of 36 gm. This disk will hold approximately 12 cc of liquid and has a porosity which allows the diffusion of trona ions into water to be complete in a reasonable time. The dimensions of the porous disk were recorded.

After the supporting wire had been attached, the dry frit was immersed in the trona solution for about 63 hours to ensure a complete filling of the pores. Only a small volume of the liquid is required to fill the disk when initially dry, but a large volume is needed to replace the liquid in a wet disk with a new liquid of different composition. When the soaking was complete, the disk was transferred to the solvent bath in the thermostat, and the run was carried out. After the trona run was complete, the disk was suspended in about 1.5 liter of 1.5 M KCl solution and allowed to soak for 45 hours. A run was then made for calibration purposes to determine the apparatus constant α .

After use, the disk was soaked overnight in distilled water to remove KCl completely and dried in air at room temperature for about 5 days.

While the frit was soaking in the solution, the solvent bath was filled and mounted in the constant temperature bath. At least 1 hour was allowed for thermal equilibrium since there was no stirring, and the temperature was checked periodically with a thermometer. In this experiment the solvent bath contained distilled water.

After the frit was adequately soaked, excess liquid was allowed to drop off, and the frit was transferred quickly to the solvent bath. The frit was suspended from a hook which was supported from one side of the

balance. The time was noted. After an initial period of 5 minutes had been allowed for transients to die out, readings of the apparent weight were taken and recorded at regular intervals. Weighings were made at 1-min intervals until the difference between successive readings was about one-fourth to one-fifth of its initial value (about 1.25 hour). Since all readings were taken at exactly 1-minute intervals, a value for $W(\infty)$ is not needed, as the data can be treated using Guggenheim's method.*

Data and calculations for this experiment are given in Tables 7 and 8. These data in terms of $\log (W(t+\Delta t)-W(t))$ versus time are fitted by a straight line using least square method. The slope of the line gives the calculated value of the diffusion coefficient for trona from a saturated solution at 25°C to water as $0.86145 \times 10^{-5} \text{ cm}^2/\text{sec}$. The reference solution for determining the diffusion coefficient was 1.5 M KCl solution made in distilled water, and its diffusion coefficient was $1.94 \times 10^{-5} \text{ cm}^2/\text{sec}$.

5.6 Discussion of Experimental Results

The results of the containers test, equilibrium test, kinetic rate constants determination and diffusion test are discussed below.

5.6.1 Results of Containers Test

These results, as shown in Table 3 and represented by Figures 7 and 8, indicate that over a period of 6 months the ratio of sodium carbonate to sodium bicarbonate in solution at ambient temperature had changed from an initial value of 1 to 2.9. This change in ratio from 1 to 2.9 indicates that trona (sodium sesquicarbonate, $\text{Na}_2\text{CO}_3:\text{NaHCO}_3:2\text{H}_2\text{O}$) is not stable in solution at ambient temperature. The results of Tables 4 and 6 are also shown in Figure 7.

*In this method quantities $[W(t + \Delta t) - W(t)]$ using a constant Δt of about 15 min were calculated, and then a plot of $\log [W(t + \Delta t) - W(t)]$ versus time yields a straight line with a slope of $(-\alpha D)$.

The results presented in Table 3 show that the 4:1, 6:1 and 8:1 solutions of sodium carbonate and sodium bicarbonate mixtures when kept open to the atmosphere approach an equilibrium ratio value between 5 and 6 while the solutions with mole ratios of 3:1 and 2:1 have changed to 3.5 and 3.6, respectively. However, the results obtained from the covered containers show a strange behavior. According to these results, the equilibrium ratio of Na_2CO_3 to NaHCO_3 is higher than their corresponding values in the uncovered containers.

5.6.2 Equilibrium Composition for Trona Saturated Solution

The results of this experiment, performed over a period of three months, as shown in Table 4 and plotted in Figure 7, show that the trona saturated solution when kept at ambient temperature with room air bubbling through it gradually decomposes and the ratio of sodium carbonate to sodium bicarbonate changes to a value equal to about 1.6 and continues to increase. Equilibrium was not reached even in 3 months. However, the ratio obtained in this test over a period of 3 months is definitely a better indication of how the ratio changes than that found in container tests, because in this test air was continuously bubbled through the solution for better air-to-liquid contact. Also, a much larger volume of solution was made in a large container in this test, and the liquid level was maintained constant by employing a water bird bath. In contrast, the volume of solution in the containers was so small that large amounts of fresh water had to be added periodically to bring them to the original volume.

5.6.3 Results of Kinetic Experiment

Reaction rate constants could not be obtained for the overall decomposition of trona as described by Equation (4) because time and funding limitations prevented employing the necessary specialized technique of analysis. The results of this experiment are shown in Table 6 and are plotted in Figure 7. However, the rate of decomposition of trona was faster in the beginning and then slows down as expected.

From the results of three different tests on trona solutions, namely containers test, equilibrium test, and kinetic test, as shown in Figure 7, it is evident that none of these solutions reached an equilibrium composition. From the least square line as shown in Figure 7, representing data of all the three tests, it appears that after six months the molar ratio of trona solutions has changed from 1.0 to about 2.8.

5.6.4 Results of Diffusion Experiment

The value of the diffusion coefficient obtained in this test for trona saturated solution at 25°C in distilled water is $0.861 \times 10^{-5} \text{ cm}^2/\text{sec}$. with a standard deviation of $\pm 26.4\%$. For comparison, the diffusion coefficient for KCl in 1.5 M solution under identical conditions is about $1.94 \times 10^{-5} \text{ cm}^2/\text{sec}$. Figure 9 shows the data and the least-square line used in the calculation of the apparatus constant, while Figure 10 represents the data and the least square line used in determining the diffusion coefficient of trona from saturated solution in water.

5.6.5 Estimation of Experimental Errors

The data represented in Table 3 indicate a good reproducibility of the sodium carbonate to sodium bicarbonate ratio by the titration technique used. The scatter between various data points obtained from the same solution is less than $\pm 10\%$ for most sets. However, for two sets it is equal to 14.2% and 12.5%.

The analysis of pure sodium carbonate (which was of about 99% purity), when analyzed by employing the titration technique given in the Appendix, indicated a Na_2CO_3 content of 94%. This indicates that the error introduced by the titration technique itself is about 5%.

From the data in Table 7, the standard deviation of the slope of the least square line ($-\alpha D_{1.5\text{MKCl}}$) is calculated. Since in this test the diffusion coefficient of 1.5 M KCl is assumed as a known quantity, the standard deviation of apparatus constant (α) is calculated. From the

data on trona solutions in Table 8, the standard deviation of the slope of the least square line ($-\alpha D_{\text{trona}}$) is calculated. From this the standard deviation for D_{trona} is calculated* because the value of α is known from Table 7.

*If $C = AB$, then $Z_C^2 = Z_A^2 + Z_B^2$ where Z of a variable (A, B, or C) is defined as the ratio of standard deviation to the mean value of the variable (Reference 16).

6.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The original motivation behind this study was to gather relevant data primarily from the published literature on the technical feasibility of using Na_2CO_3 - NaHCO_3 mixtures for a saturated solar pond. While there are ample data on mining of trona and of solid trona in equilibrium with Na_2CO_3 - NaHCO_3 solution, in Task 1 of this contract, it was discovered that very little, if any, information is available on the chemical stability of 1:1, 2:1 and 3:1 Na_2CO_3 - NaHCO_3 solutions without any solid phase. Due to this, the scope of work under this contract was slightly modified.

It was decided to generate the necessary chemistry and chemical equilibrium data in the laboratory under Task 2 of this contract. Moreover, several contacts with Allied Chemical Company, who is involved in the mining of trona for soda ash production, were made to make sure that we were not duplicating any previously published work. Because of time and funding constraints, a more thorough investigation of the problem though desirable was not possible. Based on theoretical and experimental work presented in this report, the following tentative conclusions can be drawn.

(i) Trona solution is not chemically stable either at room temperature or higher temperatures and therefore trona as such in 1:1 mole ratio is not suitable for saturated solar ponds. Nevertheless, it is an excellent candidate for unsaturated solar ponds. We have operated a stable laboratory unsaturated pond using trona for over two months.

(ii) The containers test indicates that the equilibrium composition of the system under consideration should correspond to the sodium carbonate to bicarbonate ratio of about 4 to 6, in the same range as predicted by Equation (3) given by Harte et al. (11). However, there is a lot of uncertainty in these results. Because of evaporation losses, the solution concentration in this test varied from an initial value of 15% to

about 60% when a significant amount of water had evaporated. Fresh water was added periodically to make up for the water loss before analyzing these solutions.

(iii) The covered containers test results are not conclusive as they indicate stable ratios higher than those for uncovered containers, contrary to the idea of reducing the decomposition rate due to covering.

(iv) The diffusion coefficient of trona from a saturated solution in water is $0.86 \times 10^{-5} \text{ cm}^2/\text{sec}$ with a standard deviation of 26.4%, which is about half that for sodium chloride solution under identical conditions. Thus, a trona unsaturated solar pond will need about half the amount of salt makeup than a sodium chloride pond with the same concentration gradient.

(v) A trona solution saturated at 60°C when kept between 60 to 70°C gave a ratio of sodium carbonate to sodium bicarbonate equal to about 3:8 after a period of 95 days.

(vi) In the literature it has been mentioned that sugar or gum can retard the decomposition of bicarbonate to carbonate in the mixture (9).

Recommendations for future work on this system include:

- (a) For a better understanding of the system chemistry, the determination of the equilibrium composition of trona and kinetic rate constants is highly recommended.
- (b) Testing of a laboratory saturated pond followed by a small field solar pond with a $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ mixture between 4:1 and 6:1.
- (c) Since a saturated solar pond using $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ is economically very attractive, further research work in understanding the chemistry of this system and particularly to make this solute chemically stable is very desirable. Such a study should not only explore the chemical means of suppressing the decomposition of

solute by adding a small amount of suitable chemicals but also physical techniques such as covering the pond or maintaining a higher CO₂ level above the pond surface.

- (d) As indicated earlier, we have operated a stable laboratory unsaturated pond using trona for over two months. Funding to test the stability and heat extraction capability of such a pond is strongly recommended. This could be followed up by a small field demonstration pond.
- (e) A regional applicability study to investigate the potential, economics, and end use of Na₂CO₃-NaHCO₃ solar pond systems in the U.S. should be pursued.

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7.0 REFERENCES

1. Tabor, H., "Large Area Solar Collectors for Power Production," Solar Energy, 7, No. 4, 189 (1963).
2. Weast, R. C., Handbook of Chemistry and Physics, 56th edition, CRC Press, Cleveland, Ohio, B-141 (1975).
3. Kirk-Othmer, Encyclopedia of Chemical Technology, InterScience Publisher, New York, NY, 18, 460 (1964).
4. Hill, H. E. and Bacon, L. R. "Ternary Systems. VI. Sodium Carbonate, Sodium Bicarbonate, and Water," Journal American Chemical Society, 49, 2487 (1927).
5. Waldeck, W. F., Lynn, G., and Hill, A. E., "Aqueous Solubility of Salts at High Temperatures. II. The Ternary System $\text{Na}_2\text{Cl}_3\text{-H}_2\text{O}$ from 100 to 200°C," Journal American Chemical Society, 56, 43 (1934).
6. Eugster, H. P., "Origin and Deposition of Trona," Contributions to Geology, 10, 49 (1971).
7. Freeth, F. A., "The System $\text{Na}_2\text{O-CO}_2\text{-NaCl-H}_2\text{O}$ Considered as Two-Four Component Systems," Philosophical Transaction of the Royal Society, 223A, 35 (1923).
8. Mellor, J. W. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 2, 755 (1946).
9. V. Urbain, Compt. Rend., 83, 503, 544 (1876).
10. McCoy, H. N. "Equilibrium in the System Composed of Sodium Carbonate, Sodium Bicarbonate, Carbon Dioxide, and Water," American Chemical Journal, 29, 437 (1903).
11. Harte, C. R. Jr., Baker, E. M. and Purcell, H. H., "Absorption of Carbon Dioxide in Carbonate-Bicarbonate Solutions. I. Equilibrium in System Carbon Dioxide-Sodium Carbonate-Sodium Bicarbonate-Water," Industrial and Engineering Chemistry, 25 (5), 528 (1933).
12. Sieverts and Fitzsche, Z. anorg. allgem. Chem., 1, 133 (1924).
13. Bradley, W. H. and Eugster, H. P., "Geochemistry and Paleolimnology of the Trona Deposits and Associated Authigenic Minerals of the Green River Formation of Wyoming," Geological Survey Professional Paper, 496-B (1969).

14. G. Schulze, Z. Phys. Chem., 89, 168 (1914).
15. F. T. Wall, P. F. Grieger, and C. W. Childers, J. Amer. Chem. Soc., 74, 3562 (1952); F. T. Wall and C. W. Childers, *ibid.*, 75, 3550 (1953); G. B. Taylor and F. t. Wall, *ibid.*, 75, 6340 (1953).
16. D. P. Shoemaker, C. W. Garland and J. I. Steinfeld, "Experiments in Physical Chemistry," Third Edition, McGraw-Hill Company, New York, NY (1979).
17. Perry, J. H., Chemical Engineers' Handbook, Fourth Edition, McGraw-Hill Company, New York, NY, 3-93 (1969).

TABLES

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TABLE 1
SOLUTION DENSITIES FOR SODIUM CARBONATE-SODIUM BICARBONATE-WATER
SYSTEM IN CLOSED CONTAINERS

Temperature °C	Solution			Original Complex			Region in Figure 3
	Density gm/cc	Wt% Na ₂ CO ₃	Wt% NaHCO ₃	Wt% Na ₂ CO ₃	Wt% NaHCO ₃	Solid Phases	
24.87	1.216	17.85	4.00	-	-	NaHCO ₃ , trona	A
	1.225	18.66	3.57	21.26	6.46	trona	B
	1.228	19.31	3.18	21.17	6.54	trona	B
	1.240	20.90	2.49	23.30	6.12	trona	B
	1.250	22.10	2.09	-	-	trona, Na ₂ CO ₃ ·10H ₂ O	C
30	1.216	17.52	4.45	-	-	NaHCO ₃ , trona	A
	1.225	18.43	3.92	19.98	5.87	trona	B
	1.226	18.54	3.91	20.09	5.66	trona	B
	1.239	21.00	2.65	20.45	4.80	trona	B
	1.256	23.39	1.79	24.01	2.95	trona	B
	1.269	24.30	1.47	25.88	4.32	trona	B
	1.301	27.52	0.82	29.06	3.91	trona	B
	1.307	28.09	0.76	-	-	trona, Na ₂ CO ₃ ·10H ₂ O	C
50	1.214	16.97	6.28	-	-	NaHCO ₃ , trona	A
	1.260	23.79	2.40	25.59	5.21	trona	B
	1.337	31.92	0.48	-	-	trona, Na ₂ CO ₃ ·10H ₂ O	C

TABLE 2

EQUILIBRIUM MOLE RATIOS FOR SATURATED SOLUTIONS
OF TRONA AND 3:2 SODIUM CARBONATE-SODIUM BICARBONATE
MIXTURE AS CALCULATED BY EQUATION (3)

Initial Molecular Ratio $\text{Na}_2\text{CO}_3:\text{NaHCO}_3$	Initial Normality of Na in Saturated Solution	Temperature (t)	Initial Fraction of Na as Na_2CO_3 (1-X)	Initial Fraction of Na as NaHCO_3 (X)	Equilibrium Molecular Ratio $\text{Na}_2\text{CO}_3:\text{NaHCO}_3$
1:1	2.605 N	20°C	0.67	0.33	6.38:1
1:1	4.472 N	80°C	0.67	0.33	22.6:1
3:2	2.467 N	20°C	0.75	0.25	6.15:1
3:2	5.27 N	80°C	0.75	0.25	25.15:1

TABLE 3
RESULTS OF LABORATORY TESTS ON VARIOUS SOLUTIONS
MADE FROM Na_2CO_3 - NaHCO_3

Initial Sample Description				Date	Days After Start	Molar Ratio Values		
Ratio*	Weight %	Time	Date					
1	15	1200	9/19 covered	10/01/79	12	1.20	1.20	----
				11/30/79	72	1.17	1.17	----
				12/31/79	103	1.36	1.38	----
				03/17/80	180	2.02	-----	----
1	15	1200	9/19 uncovered	10/01/79	12	1.25	1.24	----
				11/30/79	72	1.70	1.79	----
				12/31/79	103	2.01	1.92	----
				03/06/80	169	2.86	-----	----
2	15	1130	9/19 covered	10/02/79	13	2.60	2.40	----
				11/30/79	72	2.36	2.45	----
				12/31/79	103	2.66	2.68	----
				03/07/80	170	5.66	-----	----
2	15	1130	9/19 uncovered	10/02/79	13	2.03	2.01	----
				11/30/79	72	2.95	2.56	2.57
				12/31/79	103	2.79	2.92	----
				03/06/80	169	3.58	-----	----
3	15	1000	9/19 covered	10/02/79	13	2.40	-----	----
				11/30/79	72	3.37	3.82	3.40
				12/31/79	103	2.90	2.82	----
				93/07/80	170	8.13	-----	----
3	15	1000	9/19 uncovered	10/02/79	13	2.90	2.90	----
				11/30/79	72	2.95	2.94	3.28
				12/31/79	103	2.91	3.22	3.14
				03/06/80	169	3.49	-----	----
4	15	1415	12/4 uncovered	12/04/79	0	3.86	3.61	3.73
				12/31/79	27	3.94	3.82	----
				03/06/80	93	5.24	-----	----
6	15	1400	12/4 uncovered	12/04/79	0	5.32	5.47	5.54
				01/02/80	29	5.49	4.99	5.44
				03/06/80	93	5.19	-----	----
8	15	1420	12/4 uncovered	12/04/79	0	7.01	7.06	----
				01/02/80	29	6.04	6.14	----
				03/06/80	93	6.13	-----	----

* Molar ratio = moles Na_2CO_3 /moles NaHCO_3

TABLE 4
COMPOSITION AND MOLAR RATIO
OF SATURATED TRONA SOLUTION AS A FUNCTION
OF TIME AT ROOM TEMPERATURE

<u>Date</u>	<u>Time</u>	<u>Weight Percent</u>			<u>Molar Ratio</u>	<u>Comments</u>
		<u>Na₂CO₃</u>	<u>NaHCO₃</u>	<u>Total</u>		
12/20/79	14:15	7.81	6.19	14:00	1.10	Starting solution.
12/21/79	11:10	8.27	5.43	13:70	1.20	
12/24/79	9:30	8.10	5.45	13.55	1.18	Ratio seems to be increasing slowly.
12/26/79	12:00	8.25	5.50	13.75	1.19	
12/31/79	11:00	8.34	5.30	13.64	1.25	
1/8/80	11:00	8.97	5.42	14.39	1.31	
1/23/80	10:15	8.95	5.45	14.40	1.30	
3/3/80	11:00	8.73	4.24	12.97	1.63*	

* Still increasing; equilibrium was not reached in 3 months (see Figure 7).

TABLE 5
COMPOSITION AND MOLAR RATIO
OF SATURATED TRONA SOLUTION AS A FUNCTION
OF TIME AT 60-70°C

<u>Date</u>	<u>Time</u>	<u>Temp °C</u>	<u>Weight Percent</u>			<u>Molar Ratio</u>	<u>Comments</u>
			<u>Na₂CO₃</u>	<u>NaHCO₃</u>	<u>Total</u>		
12/31/79	5:10	60	11.16	8.84	20.0	1.0	Initial solution
1/9/80	10:10	69	13.86	7.94	21.8	1.38	
1/22/80	11:00	67	15.10	4.77	19.87	2.5	
3/4/80	14:00	70	12.82	2.68	15.5	3.79	

TABLE 6
DETERMINATION OF REACTION RATE CONSTANTS

<u>Time</u> <u>Hr</u>	<u>NaHCO₃</u> <u>gm-mole/liter</u>	<u>Na₂CO₃</u> <u>gm-mole/liter</u>	<u>H₂O</u> <u>gm-mole/liter</u>	<u>[CO₂]_s</u> <u>gm-mole/liter</u>	<u>Molar Ratio</u> <u>Na₂CO₃/NaHCO₃</u>
0	0.7547	0.8944	53.767	0.0449	1.18
1	0.7343	0.9131	53.918	0.0449	1.24
4	0.7293	0.9055	53.764	0.0449	1.24
5.25	0.7501	0.9058	53.64	0.0443	1.21
22.6	0.7728	0.8601	53.61	0.0410	1.11
45.85	0.7336	0.887	53.91	0.4145	1.21
71	0.7077	0.9185	53.79	0.0422	1.30
93.85	0.6902	0.9126	54.07	0.0419	1.32
168.72	0.7127	0.9375	53.93	0.0419	1.32
241.27	0.7132	0.8995	53.96	0.0419	1.26
1057.22	0.6326	0.9013	53.24	0.0372	1.42

TABLE 7
APPARATUS CONSTANT DETERMINATION FOR DIFFUSION EXPERIMENT

<u>t</u> <u>Min</u>	<u>W(t+Δt)-W(t)=ΔW_t</u> <u>gm</u>	<u>Log ΔW_t</u>	<u>(Log ΔW_t)²</u>	<u>t²</u>	<u>t(logΔW_t)</u>	<u>Comments</u>
15	0.0152	-1.8182	3.3058	225	-27.273	Diffusion coefficient of KCl in 1.5 M solu- tion = 1.94×10^{-5} cm ² /sec
30	0.0108	-1.9666	3.8675	900	-58.998	
45	0.0081	-2.0915	4.3744	2025	-94.1175	
60	0.0060	-2.2218	4.9364	3600	-113.308	
75	0.0052	-2.2840	5.2167	5625	-171.3	
90	0.0034	-2.4685	6.0935	8100	-222.165	
<u>105</u>	<u>0.0030</u>	<u>-2.5229</u>	<u>6.4650</u>	<u>11025</u>	<u>-264.9045</u>	
<u>Σt</u> = 420		<u>Σ log ΔW_t</u> = - 15.3735	<u>Σ (log ΔW_t)²</u> = 34.1593	<u>Σ t²</u> = 31500	<u>Σ t(log ΔW_t)</u> = - 972.066	

Slope of the least square line = $-\alpha D_{1.5\text{MKCl}} = -0.007882$

α = apparatus constant = $(0.007882 / (1.94 \times 10^{-5})) = 406.29$

Intercept of the least square line = - 1.7233

Standard deviation of the slope = $\sigma(-\alpha D_{1.5\text{MKCl}}) = 0.003236$

Standard deviation of the apparatus constant (α) = $\sigma(\alpha) =$

$$\frac{0.003236}{0.0000194} = 166.8$$

TABLE 8
DIFFUSION COEFFICIENT OF SATURATED TRONA
SOLUTION IN WATER AT 25°C

<u>t</u> <u>Min</u>	<u>W(t+Δt)-W(t)=ΔW_t</u> <u>gm</u>	<u>Log ΔW_t</u>	<u>(Log ΔW_t)²</u>	<u>t²</u>	<u>t(Log ΔW_t)</u>
15	0198	-1.703	2.900	225	- 8.808
30	0140	-1.854	3.437	900	- 55.620
45	0130	-1.886	3.557	2025	- 84.87
60	0103	-1.987	3.948	3600	-119.22
75	0083	-2.081	4.331	5625	-156.075
90	0074	-2.131	4.541	8100	-191.79
105	0069	-2.161	4.670	11025	-226.905
120	0050	-2.301	5.295	14400	-276.12
135	0055	-2.260	5.108	18225	-305.1
<u>Σt</u> = 675		<u>Σ Log ΔW_t</u> = - 18.364	<u>Σ (Log ΔW_t)²</u> = 37.786	<u>Σ t²</u> = 64125	<u>Σ t(Log ΔW_t)</u> = -1424.508

Slope of the least square line = $-\alpha D_{\text{trona}} = -0.0035$

Intercept of the least square line = - 1.7782

$$D_{\text{trona}} = (0.0035/\alpha) = \frac{.0035}{406.29} = 0.861 \times 10^{-5} \text{ cm}^2/\text{sec}$$

Standard deviation of the least square line = $\sigma(-\alpha D_{\text{trona}}) = 0.001708$

Standard deviation of apparatus constant $(\alpha)^* = \sigma(\alpha) = 166.8$

Standard deviation of $D_{\text{trona}} = \sigma(D_{\text{trona}})^{\dagger} = 2.273 \times 10^{-6}$

Percentage standard deviation of $D_{\text{trona}} = \% \sigma(D_{\text{trona}}) = 26.4$

* From Table 7

† See Section 5.6.5

FIGURES

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Figure 1. Solubility Of Several Salts Which Might Be Considered For A Saturated Pond

Figure 2. Phase diagram for $\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ system showing composition of different phases at one atmosphere pressure and 25°C .
Source (6)

Figure 3. Part of the system shown in Figure 2 enlarged and distorted to show conveniently the different possible evaporation paths.

Source (6)

Figure 4. Solubility and density of Sodium carbonate, Sodium bicarbonate and Trona in Water at saturated conditions.

Figure 5. Solubility and density of sodium carbonate-sodium bicarbonate mixture in the mole ratio of 3:2 as a function of temperature

Figure 6. Relation between CO₂ content of a gas and the bicarbonate quotient of a solution in equilibrium with it, saturated with respect to trona + nahcolite at temperatures ranging from 20° to 70°C.
Source (13)

Figure 7 . Change In The Molar Ratio Of Trona Solution With Time (Date From Tables 3, 4, 6)

Figure 8. Change In The Molar Ratio Of The Laboratory Test Solutions With Time (Data From Table 3)

Figure 9. Determination Of Apparatus Constant For Diffusion Experiment (Data From Table 7)

Figure 10. Determination Of Diffusion Coefficient Of Saturated Trona Solution In Water
At 20°C (Data From Table 8)

APPENDIX

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CHEMICAL ANALYSIS OF
THE SYSTEM COMPOSED OF SODIUM CARBONATE,
SODIUM BICARBONATE, CARBON DIOXIDE, AND WATER

The conversion of dry sodium bicarbonate into the normal carbonate, water, and carbon dioxide requires but a very moderate degree of heat. Complete decomposition takes place rapidly at 100° to 110°C. Gautier(1) found that no loss of weight occurs when the salt is placed in a vacuum at 25°C. At 35°C an appreciable loss had occurred at the end of four days. Therefore, it is important to do a complete chemical analysis of the sodium bicarbonate used for making trona.

Furthermore, solutions of sodium bicarbonate are far less stable than the dry salt. Rose(2) observed that a solution of sodium bicarbonate loses carbon dioxide by evaporation and leaves nearly pure normal carbonate. However, solutions of sodium bicarbonate and sodium carbonate in the molal ratio of 1:1, the combination of salts known as trona, seem to be quite stable as the solubility of trona up to 60°C has been reported in the literature. This statement has been further supported by Mr. Bean and Dr. Grancy(3) of Allied Chemical. According to them, trona is stored in open ponds without any appreciable decomposition of the salt.

For determining the correct analysis of a solution of sodium carbonate and sodium bicarbonate in water, the method used should not allow either the loss of carbon dioxide from bicarbonate to the atmosphere or absorption of carbon dioxide from the atmosphere by sodium carbonate during analysis. The hydrolytic dissociation of sodium bicarbonate, responsible for the carbon dioxide evolved, is represented by the equation:

The absorption of carbon dioxide converts carbonate to bicarbonate as:

The analysis method to be discussed here does not allow any carbon dioxide loss to, or absorption from, the atmosphere during analysis. This method, as applied to solutions containing bicarbonates, consists in adding, in excess, a known volume of standard alkali (NaOH), free from carbonate, precipitating the carbonate by addition of barium chloride, and finally titrating the excess of alkali with hydrochloric acid, using phenolphthalein as the indicator. In this method the necessary amount of barium chloride solution is first brought into a flask, then the measured volume of standard alkali is added, and finally a 10 cc. sample of the carbonate solution is run into the flask directly from the pipette.

When two or three analyses of the same solution have to be done, all the flasks are charged with the barium chloride and standard alkali, and corked. Then the carbonate solution measured from the pipette is added to each flask with as little loss of time as possible. After mixing, the flasks are tightly closed with rubber stoppers and allowed to stand a few minutes, after which the excess of alkali is titrated with decinormal hydrochloric acid using phenolphthalein as an indicator. The net amount of alkali used (that is, the whole amount added less that neutralized by acid in the final titration) is a measure of the carbon dioxide present as bicarbonate.

The reactions which occur during bicarbonate analysis are:

Where $l > n+p$

$$m > n$$

Thus the amount of sodium as bicarbonate is total NaOH added less NaOH neutralized by HCl, i.e., $m-(m-n)$.

This method allows the conversion of all bicarbonate to carbonate by NaOH and finally precipitation of all the carbonate as barium carbonate, thus there is no chance of either loss or absorption of carbon dioxide during the analysis.

In order to calculate the amounts of both carbonate and bicarbonate in any solution containing them, it is necessary to know the total amount of sodium. This is determined by titration with standard hydrochloric acid, using methyl orange as indicator, and taking for the end reaction the "normal color" produced by the indicator when dissolved in water saturated with carbon dioxide. The total amount of sodium calculated from this titration less the sodium corresponding to bicarbonate given by the first titration is equal to the amount of sodium present as a carbonate.

The reaction which occurs during analysis of total sodium as carbonate and bicarbonate is:

If there was no problem of carbon dioxide loss during analysis, analysis would have been much simpler. In that case, the contents of bicarbonate and carbonate could be analyzed by titrating the solution of carbonate and bicarbonate with standard hydrochloric acid using phenolphthalein and methyl orange both as indicators. The first end point given by phenolphthalein gives carbon dioxide present as bicarbonate, and thus sodium present as bicarbonate, while the second end point given

by methylorange gives total sodium present both as carbonate and bicarbonate. Reactions which occur during this titration are:

However, the loss of CO_2 from bicarbonate during analysis will give an error and we would not get reproducible results. Therefore, barium chloride and an excess alkali (NaOH) should be used in the analysis of a solution containing both sodium carbonate and bicarbonate, and this was the method used in our work.

REFERENCES

1. Gautier: Ber.d. Chem. Ges., 9, 1434 (1876)
2. Rose: Pogg. Annm., 34, 158 (1835)
3. Private Communication with Mr. Bean and Dr. Grancy of Allied Chemical.
4. McCoy: American Chemical Journal, 29, 437 (1903)