Anhydrous Sodium Carbonate as a Standard of Reference in Acidimetry

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During the transformation of sodium bicarbonate to sodium carbonate, moisture to the extent of approximately 0.1% is occluded within the product. This moisture is lost very slowly at temperatures even as high as 300° C. No detectable amounts of sodium hydroxide were found in samples of sodium carbonate that had been transformed at temperatures below 300° C. Samples of five leading brands of reagent grade sodium carbonate were found to have purity factors satisfactory for a standard of reference in acidimetry.

SINCE the beginning of the century sodium carbonate has been widely used as a standard of reference in acidimetry. Lunge (*7*) showed that sodium carbonate was stable when heated for a long period at temperatures as high as 300° C. At the present time there is uncertainty concerning not only the temperature and conditions under which sodium bicarbonate may be completely transformed into the normal carbonate, but also the purity of the product.

Kunz-Krause and Richter (*4*) reported that decomposition of sodium bicarbonate was only 99% complete when heated to constant weight at 250° C. but was complete when the material was stirred several times at that temperature. Smith and Hardy (*9*) found that 2 hours were required for complete decomposition of the acid salt at 305° C. at atmospheric pressure because of the slowness of the reaction

$$Na_2CO_3.H_2O = Na_2CO_3 + H_2O$$

Lunge (*6*) reported that bicarbonate is completely converted into the carbonate upon being heated for a few minutes at 260° to 270° C., and is free of bicarbonate, water, and sodium oxide after being heated for 0.5 hour at not over 300° C. More recently Lidner and Figala (*5*) reported that the reaction is complete after several hours at 130° to 140° C., and Waldbauer, McCann, and Tuleen (*10*) concluded that any sample of sodium bicarbonate heated above 150° C. is completely converted, regardless of the time of heating, and since their product was found to have a factor of purity greater than unity, that sodium hydroxide is produced during the reaction. Hou (*3*) also obtained a product (by conversion in a rotary furnace at temperatures ranging from 160° to 220° C.), the factor of purity of which was over unity.

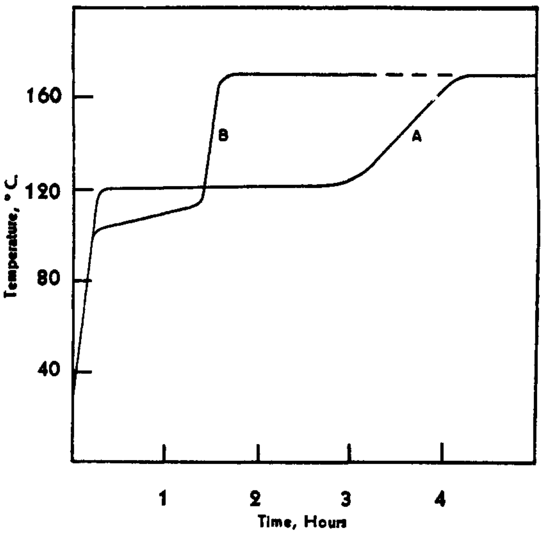

Figure 1

Many past investigations were not sufficiently precise for establishing the conditions in the preparation of a reagent to be used as a standard of reference in analysis. Whether a reaction may be considered complete may depend upon the precision used in the experimental work. In the present work precision requirements were kept in mind, with a view to clearing up the uncertainty concerning the methods of preparation and the purity of sodium carbonate.

MATERIALS AND REAGENTS

All materials and reagents were reagent grade. Three different samples of sodium bicarbonate were used: the first supplied by a well-known firm, the second prepared from this by recrystallization from hot aqueous solution, and the third prepared by saturating a solution of the normal salt with carbon dioxide. Standard hydrochloric acid solutions were made from constant-boiling acid prepared according to Foulk and Hollingsworth (*2*). Two standard acid stock solutions were prepared from independently prepared constant-boiling hydrochloric acid. A sample of sodium carbonate analyzed by one standard solution showed a factor of purity of 99.99%, and by the second solution 100.00%. The alcohol was thoroughly tested and found free from significant amounts of acid- or base-neutralizing components.

METHODS OF ANALYSIS

The purity of the sodium carbonate product was determined by titration against standard hydrochloric acid approximately 0.5 *N*. Methyl yellow modified with methylene blue (*1*) was used. All methods were designed to correspond to a precision of 1 part in 10,000. Relatively large samples were analyzed, weighing burets were used, and weights were adjusted to the vacuum basis.

Factors of purity were determined on 19 different samples involving more than 50 determinations. The average of the 19 average deviations was 1.4 parts per 10,000. The work was carried out during months when the relative humidity inside the heated laboratory was very low. When ordinary precautions were exercised the hygroscopic properties of the product were found not to interfere to any significant extent.

TIME-TEMPERATURE STUDIES

The fact that the reactions involved are endothermic suggests that the course of the reactions can be studied by following the temperature at the center of a comparatively large mass of the substance over the transformation period. Experimental conditions were as follows:

An ordinary 30-ml. (1-ounce) wide-mouthed bottle was filled with the samples, which weighed approximately 30 grams. The bottle was closed with a cork stopper through which the thermometer was inserted, so that the bulb was in the center of the sample. The cork had a small groove to allow the decomposition products to escape. The bottle was suspended horizontally in an oven, the temperature of which was thermostatically regulated. Temperature readings were taken until the temperature at the center of the sample became equal to that of the oven.

Runs were made at oven temperatures of 290°, 200°, 170°, and 130° C. The results in each case were similar. After a short rapid rise to approximately 120° C. the temperature at the center of the reaction mass remained practically constant at this temperature for periods ranging from 0.5 hour at the highest oven temperature to 8 hours at the lowest temperature, then rose rapidly to oven temperature. In each case only one constant-temperature period was found. The upper part (above 160°) of each curve for runs made at the higher temperatures was practically identical with the curve of the corresponding blank run. When samples of the product obtained from the runs at 170° and 200° were ignited in a furnace for 3 hours at 290° C., losses in weight

Table I. Time-Temperature Runs

(30-gram sample in 1-ounce bottle)

Sample	Oven Temperature ° C.	Constant Temperature ° C.	Period of Constant Temperature *Hours*
$NaHCO_3$	290	125	0.8
	200	122	2.0
	170	121	3.5
	130	118	8.0
$Na_2CO_3.H_2O$	170	112	1.5

Table II. Time for Completion of Reaction

(5-gram sample of $NaHCO_3$ in crucible)

Temperature, ° C.	140	160	200	290
Time, hours	3.0	1.5	0.5	0.4

were 0.02 and 0.01%, respectively. In the same way time-temperature runs were made on samples of sodium carbonate monohydrate, which gave a practically constant-temperature period at 112°.

Details of the time-temperature runs (Table I) and characteristic curves (Figure 1) demonstrate that the decomposition proper of sodium bicarbonate takes place at relatively low temperatures and that carbon dioxide and water are lost simultaneously. The rate of decomposition increases rapidly with increase in the temperature, so that the reaction is practically complete by the time the entire sample has reached 160° C.

OPTIMUM CONDITIONS FOR PREPARING PURE SODIUM CARBONATE

In determining the optimum methods for producing pure sodium carbonate, easily reproducible experimental conditions were selected.

An approximately 5-gram sample of bicarbonate was placed in a 20-ml. crucible. For temperatures up to 220° C. an oven was used; above that an ordinary ignition furnace. The crucible was placed in the oven without cover and out of direct contact with the heating element or its radiations. Preliminary runs were made to determine the time of heating necessary for completion of the reaction at several temperatures ranging from 140° to 300°. The completeness of the reaction was determined by ascertaining the loss in weight upon further ignition for 3 hours at 300°. Later results indicated that ignition at 300° C. does not necessarily result in a completely dehydrated product, but for the purposes of this investigation this test was adequate.

In every case decomposition came to practical completion from 140° to 280° C. with some dispatch; following this was a period in which the samples lost weight slowly. Practically identical results were obtained in more than 50 ignitions on three different samples of sodium bicarbonate. The time necessary for consummation of the fast reaction for several temperatures is given in Table II. The amount of the "slowly lost" weight approximated 6 parts per 10,000. The work of Richards and Hoover (*8*) indicates that this slowly lost weight consists of moisture occluded in the crystals of the products.

To test the validity of this, several samples of sodium carbonate previously ignited at 300° C. were moistened with water, dried at 140°, and reweighed. During the process the samples became caked and gained an average of 0.02% in weight. This responded to ignition in much the same way as the slowly lost portion of the decomposition product of the bicarbonate.

Up to this point identical results had been obtained for each of the three samples studied. For the remainder of the work one sample only was used, that supplied by a well-known firm.

As the amount of slowly lost weight is roughly independent of the method used for preparing the acid salt, one may conclude that it consists of moisture occluded in the crystals of the product. Since it resists complete elimination at temperatures as high as 300° C., a study was made of effective ordinary means for eliminating most of the occluded moisture. It was found that pulverization of the product was helpful, and that after being thoroughly ground in an agate mortar the product became substantially constant in weight after 1 hour ignition at 140° C. and above. All the moisture is not eliminated at these temperatures, however, since upon further ignition at 270° C. the pulverized product dried for 1 hour at 140° lost an additional 0.02%, while that dried at 200° lost an additional 0.01%. These later ignitions were all carried out in weighing bottles with well-fitted glass stoppers since the desired precision could not be obtained when an ordinary covered porcelain crucible was employed.

The factor of purity of the product obtained from the first sample mentioned above at each of several transformation temperatures was determined by titration against standard hydrochloric acid. The results of nine analyses involving 18 determinations are given in Table III. The largest average deviation of the series was 0.02% and the author believes that the uncertainty in any case is no greater than this amount. These results verify the fact that transformations at temperatures below 300° C. produce a product containing less than 0.1% of moisture and that this moisture may be partially eliminated by pulverization of the sample and reignition.

Table III. Purity of Sodium Bicarbonate Transformation Product

Sample No.	Transformation Temperature ° C.	Time *Hours*	Product Ground	Reheating Temperature ° C.	Na_2CO_3 %
1	180	2	No	...	99.92
2	220	2	No	...	99.92
3	220	12	No	...	99.95
4	270	1	No	...	99.91
5	270	4	No	...	99.94
6	220	12	Yes	220	99.99
7	200	1	Yes	160	99.95
8	200	1	Yes	200	99.96
9	200	1	Yes	270	99.97

Table IV. Extraction with Alcohol

Conversion Temperature	Sodium Carbonate	
	Before extraction	After extraction
° C.	%	%
165	99.93	99.93
200	99.93	99.94

DETERMINATION OF SODIUM HYDROXIDE CONTENT

These results included nothing that would suggest the presence of sodium hydroxide in the product transformed at temperatures below 300° C. A complete investigation, made to determine whether there were significant traces of sodium hydroxide in the product produced at the several temperatures, comprised two parts: analysis of the product before and after extraction with alcohol, and analysis of the alcoholic extract.

A sample was placed in a 50-ml. narrow-mouthed flask, 20 ml. of alcohol were added, and the mixture was allowed to stand for several hours with infrequent shaking. The clear liquid was carefully but rapidly decanted into another 50-ml. flask, 20 ml. of carbon dioxide-free water were added, and the liquid was immediately titrated with 0.05 *N* hydrochloric acid, using phenolphthalein indicator. In case a trace of sodium carbonate was carried over during the first decantation, a second served to ensure a perfectly clear solution.

Numerous extractions were carried out on the products of decomposition at the several temperatures, on products previously extracted with alcohol (blanks), and on samples of reagent grade sodium carbonate obtained from five producers of pure chemicals. The titer in each case was small, and within the limit of error of the titration, the same for every sample extracted and independent of the weight of the sample. Two samples of sodium carbonate transformed from sodium bicarbonate by ignition for 24 hours at 200° and 165° C., respectively, were analyzed before and after extraction with alcohol. Results in Table IV demonstrate that sodium carbonate transformed from the acid salt at temperatures below 300° C. contains no measurable amounts of sodium hydroxide extractable with alcohol.

Finally, to determine the purity of reagent grade sodium carbonate obtainable on the market, samples of five leading brands were dried in the oven at 140° for 1 hour and analyzed by titration against standard hydrochloric acid, with the following results: 99.99, 99.98, 100.00, 99.99, and 99.98%. This demonstrates that reagent grade sodium carbonate ordinarily obtainable is pure enough to meet even the most exacting requirements as a standard in acidimetry.

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Laboratory Distillation at Atmospheric Pressure of Normally Liquid Hydrocarbons

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The factors involved in the laboratory distillation of normally liquid hydrocarbons when it is desired to separate near-boiling components are discussed and suitable fractionating columns are described. In a generally useful column the fractionating section is packed with single-turn wire helices, the column being insulated with an especially designed electrical heater which makes it possible to maintain the fractionating section in an adiabatic condition. This column is equipped with a special head provided with electrical means for automatically maintaining the desired reflux ratio. Columns of this design containing up to about 100 equivalent theoretical trays have been found to operate satisfactorily.

DURING the past decade much work has been done on the design of laboratory fractionating columns, particularly with respect to the development of efficient packing materials. Highly efficient column packings have been developed and incorporated in the fractionating columns described by Baker (*1*), Bruun (*2*, *3*), Fenske (*6-9*), Podbielniak (*17*), Selker (*20*), and Stedman (*21*).

The factors involved in the selection of a column packing have been discussed by Ward (*24*). In general, a good packing should present a large area to effect efficient contacting of liquid and vapor, and should have a high percentage of free space, since this permits high vapor velocities with resulting high throughput. In addition, it should pack uniformly into the distilling tube to minimize channeling and flooding difficulties. From the latter standpoint symmetrically shaped packings are to be preferred over irregular shapes.

In addition to an efficient packing, the fractionating section must be suitably insulated against gain or loss of heat. The loss of heat to the surroundings results in internal reflux which reduces the capacity of the column and may also decrease column efficiency if the amount of such reflux is large. The heat capacity of the insulating jacket should be as low as possible in order to decrease the time required for the column to come to equilibrium. Low heat capacity also tends to reduce flooding troubles sometimes encountered when a component having a considerably higher boiling point begins to move up the column. Suitable heat insulation may be obtained with vacuum jackets equipped with metal reflecting shields, or with suitable lagging and electrical heating.

The type of distilling head used has much to do with the stable operation of the column. The total condensation type is preferred to partial condensation types because of the critical control required by the latter. The somewhat increased efficiency which may sometimes be obtained with partial condensation types is usually more than offset by their irregular operation, which tends to keep the column from reaching equilibrium. In addition, the still-head design should embody means for maintaining steady volumes of reflux and product.

The operation and degree of control required of a fractionating column naturally vary with the kind of sample being analyzed and the separation desired. For very close cutting it is essential that column operation be smooth and that once the column has reached equilibrium nothing be done to disturb this equilibrium. This involves close control of the heat input to the kettle, accurate control of reflux ratio and product take-off rate, and maintenance of adiabatic conditions over the fractionating zone of the column. In addition, it is essential to keep the kettle liquid actively boiling. If this is not done the lighter components may become exhausted from the surface while considerable amounts still remain in the lower parts of the kettle liquid, thus producing false "breaks".

The behavior of fractionating columns may be shown visually by fractionating mixtures of propane, butane, and diazomethane, a yellow compound boiling at −23° C., in glass columns. Such studies illustrate vividly the difficulty with which the last traces of light material are removed from the kettle, and the time required to re-establish equilibrium after momentary upsets caused by irregular operation.

DESCRIPTION OF FRACTIONATING COLUMN

In Figure 1 are shown details of the construction of a column which has been found to be stable in operation, and to require but little attention. It is capable of giving very good fractionation with a wide variety of samples.

Both metal and glass columns have been constructed. The type most generally used is a glass column with a packed section from 60 to 180 cm. long with an inside diameter of from 1.2 to 3.1 cm.

The packing material used is generally $^1/_{16}$- or $^3/_{32}$-inch single-turn helices made of Nos. 36 and 30 wire, respectively, of the type described by Fenske (*8*). This packing is available in a wide variety of metals and alloys. Usually rings made of 18 chromium–8 nickel are preferred, since the metal has good corrosion resistance and can be readily cleaned with strong acids. According to Whitmore *et al.* (*25*) the HETP of this type of packing varies with the diameter, height, and throughput or boil-up rate. For 2.5 cm. and smaller columns the HETP is in the range of 1.5 to 3 cm. The maximum throughput or boil-up rate for a 2.0 cm. inside diameter column packed with $^3/_{32}$-inch helices made of No. 30 wire is in the range of 1200 to 1300 cc. per hour, which correspounds to a vapor velocity of about 24.0 cm. per second. Proper installation of the packing is essential for highest throughputs. The tamping method described by Fenske has been found satisfactory. If the column is improperly packed, so that there are zones of close packing and zones of loose packing, flooding is likely to occur in the column at relatively low