months old are given in Table I. All filtrations were carried out by gravity, without suction and without access of carbon dioxide. Pressure was obtained by maintaining a fairly high column of lye over the filtering medium.

Oil lye can be conveniently settled and stored in paraffinlined bottles until needed. Preference should be given to the centrifuge method rather than the heating method, when oil lye must be clarified in a short time.

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Anhydrous Sodium Carbonate as a Standard of Reference in Acidimetry

Stability of Sodium Carbonate in the Temperature Range 300° to 400° C.

G. FREDERICK SMITH AND G. F. CROAD, University of Illinois, Urbana, Ill.

THE generally accepted procedure for the preparation of anhydrous sodium carbonate by the conversion of pure sodium bicarbonate calls for decomposition at 300° C. Waldbauer, McCann, and Tuleen (3) state that this conversion can be carried out at temperatures from 102° to 450° C. The wide difference between the previously accepted maximum temperature of 300° C. and the findings of Waldbauer and collaborators (3) has led to the present investigation.

Preparation of Materials

Constant-Boiling Hydrochloric Acid. This was made by the process described by Foulk and Hollingsworth (1), and the distillation flask and condenser as well as the pressure-regulating apparatus were exact duplicates of those which they described. Since but two fractions of distilled acid were desired, the receiver was modified as shown in Figure 1. By its use the first 400 ml. of distillate were collected with the receiver in position as shown in Figure 1. The last portion of distillate, 50 ml. of constantboiling acid, was collected in the smaller of the two receivers after the receiving flasks had been inverted without discontinuing the process of distillation. The constant-boiling hydrochloric acid was taken at 750-mm. pressure, after correcting the existing barometric reading with the pressure-regulating system as shown. A 5000-ml. flask was placed between the acid receiver from the still and the pressure-regulating device to minimize fluctuations in the water manometer shown. Ten grams of platinum scrap were used in the distilling flask to prevent bumping, the distillate was collected at a rate of 4 to 5 ml. per minute as recommended, and 50 ml. of undistilled acid were left in the still.

ANHYDROUS SODIUM CAR-BONATE. Pure sodium bicarbonate was dissolved in pure water to make a saturated solution at 80° C., which was filtered and allowed to cool. The sodium bicarbonate thus obtained was centrifuged and dried at approximately 50° C. Qualitative tests showed the absence of chloride, sulfate, potassium, etc. Anhydrous sodium carbonate was prepared from the bicarbonate by the process described by Smith and Hardy (2). The sodium bicarbonate was dis-sociated at 290° C. at 1- to sociated at 290° C, at 1- to 4-mm, pressure during a period of 1 hour and stored in glass-stoppered bottles in a designed bottles in a desiccator over anhydrous magnesium perchlorate. The apparatus assembly for this preparation is shown in Figure 2.



FIGURE 1. APPARATUS FOR PREPARATION OF CONSTANT-BOILING HYDROCHLORIC ACID

APPROXIMATELY 0.2 N Hydrochloric Acid. Portions of constant-boiling hydrochloric acid were weighed from weight burets, transferred to calibrated volumetric flasks, and diluted to volume.

Experimental Procedure

The purity of the anhydrous sodium carbonate was first experimentally demonstrated. Weighed portions of anhydrous sodium carbonate (corrected to the vacuum basis) were weighed into 400-ml. beakers, dissolved in water, and titrated, using the standard hydrochloric acid and Bureau of Standards calibrated burets. The agreement between the calculated normality of hydrochloric acid and the values found by this method, assuming the anhydrous sodium carbonate to be pure, is indicated by the following series of results:

0.2320 0.2320 0.2322 0.2319 Av. 0.2320 (calcd. 0.2318) 0.2005 0.2003 0.2000 0.2002 Av. 0.2002 (calcd. 0.2002)

The results show an agreement to within less than 0.01 per cent of theory, and are typical of results obtained from 10 different solutions of standard hydrochloric acid from different samples of prepared constant-boiling acid. The indicator used in these titrations was an aqueous solution of 0.10 per cent methyl orange and 0.25 per cent indigo carmine. The color change is from green in basic solution to gray at the end

> point and violet in acid solution. It is concluded that the anhydrous sodium carbonate was pure as prepared.

Change in Alkaline Value

Samples of the same preparation of anhydrous sodium carbonate were heated for 4 hours at various temperatures between 300° and 390° C. and used to standardize a given solution of standard hydrochloric acid made from constant-boiling material as described.

The results, shown in Table I, are averages from at



APPARATUS FOR PREPARATION OF ANHYDROUS FIGURE 2 SODIUM CARBONATE FROM BICARBONATE

least two closely agreeing duplicates. At 390° C. the error in the determination of acid normality is 3 per cent for the 4-hour time of decomposition. By plotting the data of Table I with temperature on one axis and acid normality on the other, it is seen that an approximate straight-line relationship is involved. There is no reason to believe that at 475° C. the error involved in a 4-hour treatment would not double the inaccuracy to approximately 6 per cent or more.

TABLE I. INFLUENCE OF TEMPERATURES BETWEEN 300° AND 390° C. ON ALKALINE VALUE OF ANHYDROUS SODIUM CARBONATE (Time of heating 4 hours at indicated temperature. Normality of HCl used

Temperature	Normality of HCl	Change in HCl
°C.	Found	Normality
300 330 370 380 390	$\begin{array}{c} 0.2121 \\ 0.2097 \\ 0.2075 \\ 0.2070 \\ 0.2061 \end{array}$	0.0000 0.0024 0.0046 0.0051 0.0060

Determination of Decomposition

The experiments of Table I are repeated at a temperature of 390° to 400° C, with intervals of 0.25 to 3 hours. In this case a stream of dry, carbon dioxide-free air was passed over the sample and the evolved gases containing carbon dioxide of decomposition were then passed through ascarite and anhydrone in a weighed Turner tube to absorb evolved carbon dioxide. The loss in weight of the sample was also determined as a check. The results, shown in Table II, indicate a fair degree of agreement between the loss in weight of samples and the recovered weight of carbon dioxide evolved. With longer time intervals the rate of evolution of carbon dioxide seems to accelerate, possibly because of the effect of accumulation of sodium oxide as impurity. The time of reaction was not sufficiently extended to substantiate this point.

STUDIES IN CLOSED SYSTEM. The experiments of Table II were repeated with the changed condition that the system was kept closed until the end of the time interval involved and was then flushed out with a stream of dry, carbon dioxidefree air, and the carbon dioxide evolved was then absorbed and weighed. The rate of decomposition would in this case be expected to diminish as the accumulation of carbon dioxide increased. This was found to be the case, as shown in Table III.

An examination of Table III and comparison with Table II show that the rate of decomposition in a spacious closed system is about equal to that in a system in which the evolved carbon dioxide is removed rather than allowed to accumulate. Only at the 3-hour period of heating is the rate lessened. A graph of these data shows a rapid decrease in the change of evolution of carbon dioxide with increase in time, indicating that the vapor pressure of sodium carbonate at 400° C., which results in the evolution of carbon dioxide, does not appreciably retard the rate of decomposition until sufficient has accumulated. This effect is governed by the volume of the decomposition chamber.

TABLE II.DECOMPOSITION OF SODIUM CARBONATE AT 390° to 400° C. AT VARIOUS TIME INTERVALS							
(As determined by los	s in weig	ht and we	eight of C	O2 evolved	l.)		
Weight of Na ₂ CO ₃ , gram Time heated, min. Weight of Na ₂ CO ₂ after	$\begin{array}{c} 0.7569 \\ 15 \end{array}$	0.7564 30	0,7107 60	$\substack{0.9116\\180}$	0. 7414 360		
Weight loss, gram Weight of CO ₂ found, gram	$\begin{array}{c} 0.7552 \\ 0.0017 \\ 0.0017 \end{array}$	$\begin{array}{c} 0.7534 \\ 0.0030 \\ 0.0032 \end{array}$	$0.7070 \\ 0.0037 \\ 0.0036$	$0.9064 \\ 0.0052 \\ 0.0063$	$0.7285 \\ 0.0129 \\ 0.0117$		
Av. per cent decomposition	0.23	0.40	0.51	0.63	1.66		
TABLE III. DECOMPOSITION OF SODIUM CARBONATE AT 390° TO 400° C. AT VARIOUS TIME INTERVALS IN A CLOSED SYSTEM							
(As determined by loss in weight and the weight of CO_2 evolved.)							
Weight of Na ₂ CO ₃ , gram Time heated, mín. Weight of Na ₂ CO ₂ after	$\begin{array}{c} 0.5733 \\ 15 \end{array}$	0.6687 30	0.6590 60	0.7744 180	0.8902 360		
weight of CO ₂ found, gram	$\begin{array}{c} 0.5716 \\ 0.0017 \\ 0.0015 \end{array}$	$\begin{array}{c} 0.6654 \\ 0.0030 \\ 0.0032 \end{array}$	$\begin{array}{c} 0.6552 \\ 0.0038 \\ 0.0046 \end{array}$	$0.7688 \\ 0.0056 \\ 0.0062$	$\begin{array}{c} 0.8831 \\ 0.0071 \\ 0.0072 \end{array}$		
Av. per cent decomposition	0.28	0.46	0.64	0.76	0.80		

The experiments of Table II were repeated at a temperature of 310° to 315° C., to test the possibility of heating sodium carbonate at a temperature above 300° C., which is the upper limit permissible according to Smith and Hardy (2) and many other investigators. Samples of approximately 1 gram lost in weight 0.0012 and 0.0015 gram, and the carbon dioxide evolved weighed 0.0014 and 0.0016 gram, respectively. A solution of 0.2120 N hydrochloric acid was restandardized, using these samples, and the values 0.2096 and 0.2091 N were found.

Conclusions

From the experimental evidence it is to be concluded that anhydrous sodium carbonate dissociates to give off carbon dioxide gas at temperatures above 300° C. Heating for 1 hour at 310° to 315° C. results in an error of more than 1 per cent in the alkaline value of the sodium carbonate so treated. Heating at temperatures up to 400° C. greatly increases the error, using either an open or closed vessel for the decomposition. The authors cannot agree with Waldbauer, McCann, and Tuleen (3) that anhydrous sodium carbonate can be heated to 475° C. without alteration in neutralization equivalent. The dynamic method of determining the carbon dioxide pressure of sodium carbonate heated above 300° C. proves that there is an appreciable decomposition and that the resulting product is not suitable for use as an acidimetric standard. Anhydrous sodium carbonate, such as that prepared for this investigation from sodium bicarbonate with vacuum dissociation at 300° C., is suitable for use in acidimetry.

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