

STANDARDIZATION OF ACIDS WITH CARBONATES AND WITH BICARBONATES.

JAMES H. RANSOM, JAMES MILLIKIN UNIVERSITY,
DECATUR, ILLINOIS.

The original purpose of the investigation was to compare the results of standardizing acids with carbonates and bicarbonates. Usually the instructions are to convert a good grade of the bicarbonate into carbonate and with the latter as primary standard titrate the acid against a known weight of it. The method is time-consuming and, in the hands of inexperienced students at least, is not always satisfactory. Any inaccuracy has been thought to be due to incomplete conversion of the bicarbonate during the heating. If the purity of the bicarbonate could be relied upon it would seem to be a better method to titrate directly with the bicarbonate. The reason for not doing so has probably been due to the belief that the purity of the bicarbonate could not be relied upon. It occurred to the author to compare the results in the normality of some acid by titrating it against a number of bicarbonates and the carbonates made from them. And since in the titration of carbonates they are first converted completely into bicarbonates, using phenolphthalein as indicator, when one-half the total volume is used it seemed desirable to observe whether the change in color of indicator occurred when one-half of the total volume was used. The results were so different from the theory that it seems desirable to include data on both points. In the titration of carbonates phenolphthalein was used in the first half and methyl orange in the second part. With bicarbonates only the latter indicator was used.

The preliminary work was carried out with a fairly good grade of sodium bicarbonate, and was titrated with sulphuric acid of nearly two normal. While the results were in the same direction as those obtained later with purer material and a more dilute acid it is felt that the possible errors are so great as to warrant their not being included in the published report. It was soon seen that it would be necessary to establish the normality of the acid to be used by some independent method. Consequently a solution of

hydrochloric acid of approximately two-tenths normal was prepared and its strength accurately determined as follows: Duplicate samples of silver nitrate, of high purity were precipitated with excess of hydrochloric acid and the weight of the silver chloride compared with that of the nitrate. The ratio, $\text{AgNO}_3 : \text{AgCl}$ in the duplicates was 1: .8434 and .84367. Theory for pure silver nitrate is .84377. A standard solution of this nitrate was then prepared and the solution titrated against a solution of sodium chloride made by dissolving 5.846 gms of very pure salt in a liter of solution. As a result of nine closely agreeing titrations the normality of the salt solution was found to be .1005 using two-tenths normal silver nitrate, and .10007 against one-tenth normal silver nitrate. The two-tenths normal silver solution, considering it to be exact within experimental error, was then titrated against the acid solution previously prepared, after neutralizing the acid with sodium hydroxide, using potassium chromate as indicator. The average of ten closely agreeing results gave a normality of .194 for the acid. With this acid and a sample of "certified" sodium bicarbonate, obtained especially for the purpose, the following work was carried out. At first, ordinary distilled water was used as solvent for the bicarbonate, the volume being indefinite but between 200 and 350 cc for each determination. Later the water was freshly boiled but not measured; and finally accurately measured volumes of the freshly distilled and cooled water were used and protected with sodium hydroxide from absorption of carbon dioxide. With each table the conditions are indicated. The bicarbonate was dried at 50° to 70° and tested for alkali reaction with phenolphthalein, (p. p below) giving negative results. In titrating the burette was filled to the zero mark for each

TABLE I.
ORDINARY DISTILLED WATER IN INDEFINITE VOLUMES.
Methyl orange (M. O.) used as indicator.

Exp. No.	Wt. of NaHCO_3	Vol. HCl M. O.	Wt. NaHCO_3 per cc HCl	Normality found
1.....	.5625	35. 1	.0160256	.1908
2.....	.5733	35. 7	.0160588	.1911
3.....	.4778	29. 8	.0160335	.1909
4.....	.3905	24. 33	.0160501	.1910
5.....	.2867	17. 94	.0159816	.1902
6.....	.3962	24. 6	.0161057	.1917
7.....	.3834	23. 85	.0160755	.1913
8.....	.3371	20. 95	.0160907	.1915
9.....	.3638	23. 00	.0160130	.1906
Average of 9 results.....			.0160483	.1910

titration and nearly the same volume used in order to eliminate errors due to inexact calibration.

While these titrations were being carried out a quantity of the same bicarbonate was heated in a sand bath to 300 until constant weight was secured. 8.9597 gms. bicarbonate on heating two days lost 3.2980 gms. The theoretical loss for the pure carbonate is 3.3065 or .09 of one per cent more.

TABLE II.

TITRATION OF SODIUM CARBONATE MADE FROM THE BICARBONATE USED ABOVE. ORDINARY DISTILLED WATER, INDEFINITE VOLUMES.

Exp. No.	Wt. of Na ₂ CO ₃	Vol. HCl P.P.	Vol. HCl M.O.	Ratio P.P.:M.O.	Vol. HCl Total	Normality found	Average
1....	.2056	10.05	10.75	1:1.07	20.8	.1865	
2....	.2477	12.10	12.70	1:1.05	24.80	.1884	
3....	.2695	13.40	13.60	1:1.01	27.00	.1883	.1877
Freshly boiled, distilled water, indefinite volumes.							
4....	.3085	14.95	15.85	1:1.06	30.80	.1889	
5....	.2634	12.50	13.55	1:1.08	26.05	.1907	
6....	.2981	14.65	14.90	1:1.01	29.55	.1903	
7....	.2924	14.22	14.68	1:1.03	28.90	.1908	
8....	.2895	13.80	14.90	1:1.07	28.70	.1903	.1902
200cc of freshly boiled, distilled water was used.							
9....	.3290	16.51	16.05	1: .97	32.56	.1906	
10....	.2771	13.62	13.78	1:1.01	27.40	.1908	
11....	.2634	12.77	13.23	1:1.03	26.00	.1911	.19083
300cc of freshly boiled, distilled water was used.							
12....	.2898	13.40	15.00	1:1.12	28.40	.1925	
13....	.2184	10.45	11.05	1:1.06	21.50	.1916	
14....	.3180	14.65	16.60	1:1.13	31.25	.1920	.19203
400cc of freshly boiled, distilled water was used.							
15....	.1895	9.35	9.77	1:1.04	19.12	.1895	
16....	.3583	17.10	18.10	1:1.05	35.20	.1920	
17....	.2258	10.70	11.70	1:1.09	22.40	.1910	
18....	.2244	10.60	11.55	1:1.09	22.15	.1911	.1909
Average ratio of volumes, P.P.:M.O.				1:1.054			

Data for potassium carbonate and the bicarbonate. In tables 3 and 4 ordinary chemically pure potassium carbonate was used after heating it for some time to 255° and allowing it to cool in a desiccator. For table 3 the acid used was approximately one-tenth normal while in table 4 the acid was approximately two-tenths. Since the problem now was to study the relative volumes in the first half of the titration (phenolphthalein as indicator) as compared with the last half (methyl orange as indicator) the exact normality of the acid was not important. In the first experiment of table 3 and the last three experiments of table 4 ordinary distilled water was used. In the others freshly boiled distilled water was employed as solvent for the car-

bonate. In experiment 1 of table 3 the volume for the phenolphthalein titration is evidently far wrong though the total is only slightly too high. For some reason the relative volumes in the two parts of the titration are not constant as would be expected. This part of the work was done in the first part of the investigation and it is possible that the end point for phenolphthalein was not as accurately judged as in later work.

TABLE III.

Exp. No.	Wt. of K ₂ CO ₃	Vol. HCl P.P.	Vol. HCl M.O.	Ratio P.P.:M.O.	Vol. HCl total	Normality found	Average
1.....	.5131	32.31	42.49	74.8	.09941	
2.....	.1766	12.4	13.5	1:1.09	25.9	.09881	
3.....	.1411	9.58	11.32	1:1.19	20.90	.09785	
4.....	.1230	9.2	9.05	1: .98	18.25	.09767	
5.....	.0768	5.45	6.3	1:1.15	11.75	.09474	

Disregarding the last which is far too low the average normality is .09843, and the greatest variation from this is one per cent.

TABLE IV.

Exp. No.	Wt. of K ₂ CO ₃	Vol. HCl P.P.	Vol. HCl M.O.	Ratio P.P.:M.O.	Vol. HCl total	Normality found	Average
1.....	.2706	9.00	9.5	1:1.06	18.5	.2119	
2.....	.3545	11.7	11.8	1:1.00†	23.5	.2180	
3.....	.2138	7.2	7.2	1:1.00	14.4	.2152	
4.....	.2126	7.00	7.2	1:1.03	14.2	.2169	
5.....	.3509	10.9	12.6	1:1.15	23.5	.2164	
6.....	.3023	9.6	10.4	1:1.08	20.00	.2190	
7.....	.4160	12.2	15.5	1:1.27	27.7	.2176	.2164

If No. 1 is omitted the average normality is .2172, and the greatest variation from this average is less than one per cent, while the variation between the lowest and highest is less than two per cent. In the first four experiments of this table the volumes in the two parts of the titration are nearly the same, and much nearer than in any of the rest of the work. They are within experimental error of what theory demands.

The following work was done with potassium carbonate made by heating to 300°, the highest grade of purity of the bicarbonate. In the first four experiments ordinary distilled water was used as solvent. With the others freshly boiled water was used. The carbonate is quite deliquescent and so after heating the carbonate was cooled in a closed weighing bottle enclosed in a desiccator. The acid used had a normality .194.

TABLE V.

Exp. No.	Wt. of K ₂ CO ₃	Vol. HCl Phe. Phth.	Vol. HCl M.O.	Ratio P.P.:M.O.	Vol. HCl total	Normality found	Average
1.....	.4029	14.3	16.2	1:1.15	30.5	.1908	
2.....	.6444	23.8	25.15	1:1.05	48.95	.1904	
3.....	.2522	8.82	10.72	1:1.21	19.54	.1870	
4.....	.4690	17.08	18.52	1:1.08	35.60	.1911	
5.....	.5098	18.30	20.50	1:1.12	38.80	.1904	
6.....	.3588	13.15	14.15	1:1.07	27.30	.1904	
7.....	.3010	11.00	12.20	1:1.11	23.2	.1880	
8.....	.3614	13.30	14.10	1:1.06	27.4	.1911	
9.....	.4094	14.9	16.10	1:1.07	31.00	.1914	.19007

Average of the last four in which the water had been boiled, .19025. Omitting the two which are abnormally low, for some unknown reason, the average of the seven is .1908. In every case the volume of acid in the first part of the titration is appreciably less than in the second part. The volume in the second part is quite consistently nearly 1.1 times that of the first part. The notable exception is where the calculated normality is unusually low indicating that the volume used was too high, possibly in the second part.

The following titrations of the acid (used above) were made directly with the potassium bicarbonate from which the carbonate used in table 5 was prepared. Ordinary distilled water was used as there seems no reason why free carbonic acid in the water should effect the volume of acid needed.

TABLE VI.

Exp. No.	Weight KHCO ₃	Volume HCl	Wt. perc HCl	Normality found	Average
1.....	.9263	48.5	.019099	.1910	
2.....	.5832	30.6	.019059	.1906	
3.....	.7194	37.6	.019133	.1913	
4.....	.4554	23.72	.019198	.1919	.1912

Discussion of results:

The normality of acids as determined from titration against either carbonates or bicarbonates, at least this is true for dilute solutions of hydrochloric acid, has a smaller value than when determined from precipitation methods. In the case at hand the normality of hydrochloric acid as determined from precipitation of silver chloride, or when titrated against standard silver nitrate had a normality of .194. When titrated against either sodium bicarbonate or potassium bicarbonate the normality found was .191; and

when either of the carbonates, made from the bicarbonates, was used the normality was slightly less. Not only was the average less, but not one of the single determinations equaled the theoretical value, .194.

In titrating carbonates in the presence of two indicators, phenol phthalein for the first action, $\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}$, and methyl orange for the second action, $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{H}_2\text{CO}_3 + \text{NaCl}$, in all but two or three titrations the volumes in the second part were larger by 1.05 to 1.1 times, though the agreement was not close in the various cases. The normality of the acid calculated on the basis of the first part of the titration of sodium carbonate with phenol phthalein was on the average .1957, or slightly more than the theoretical, .194. The lowest value was .190, and the highest, .203. With potassium carbonate the corresponding average was .1996, the lowest again being .196 and the highest .207.

Conclusions:

If any conclusions are justifiable from the data presented they seem to be the following:

1. The normality of acids as found from the titrations of either carbonates or bicarbonates is below the real normality.
2. The normality found through the bicarbonates is slightly above that found through the carbonates.
3. The normality found through that part of the titration in which phenol phthalein is used as indicator is slightly above the real normality. This seems to mean that the volume of acid used in this part is less than that needed to convert the carbonate into the bicarbonate, while the volume needed to convert the bicarbonate into carbonic acid is considerably too much. The question arises, therefore, whether these indicators are the proper ones to determine the end point in carbonate titrations.
4. The water used as solvent for the carbonates should be free from carbon dioxide. At least more consistent results are secured if it is.
5. The volume of water used as solvent, beyond a reasonable minimum, does not greatly affect the result.