kindly advice and assistance, and I wish to express my grateful thanks to him and acknowledge the many favors shown me.

STANFORD UNIVERSITY,
January 31, 1905.

Note.—The methods employed for the purification of the ammonia used in these experiments precludes the possibility of the presence of objectionable quantities of impurities other than possibly pyridine and its homologues. Tests for pyridine, by the method of H. Ost[1] failed to show more than traces of that substance in the liquid, which was not so highly purified as that used for the boiling-point determinations.

Franklin and Kraus[2] have shown the boiling-point elevation constant of ammonia to be 3.4, a value smaller than that of any other known liquid, whence it follows that nearly 3 per cent. of pyridine by weight must be present to produce a change in the boiling-point of the solvent of 0.1 degree. Since tests have shown that nothing approaching such a quantity was present, the conclusion is justified that the value given in this paper for the boiling-point of liquid ammonia can not be appreciably in error from the presence of impurities in the ammonia used.

I am indebted to Dr. William A. Noyes for the suggestion that tests for pyridine be made.

H. D. GIBBS.

FOOD LABORATORY,
SAN FRANCISCO, CALIFORNIA,
June 12, 1905.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, NO. 58. SENT BY H. W. WILEY.]

CHEMICAL GLASSWARE.

BY PERCY H. WALKER.

Received April 28, 1905.

It is unnecessary to call the attention of the analytical chemist to the fact that all glass is more or less soluble in water and in various solutions. He simply accepts the fact and when working with the greatest care avoids, as far as possible, the use of glass. Of really greater practical importance than the difference in solu-

[1] "Commercial Organic Analysis," Allen, Vol. III, Part II, p. 104.

[2] *Amer. Chem. J.*, **20**, 846 (1898).

bility of different kinds of glass is the difference they show as regards breaking and cracking by changes of temperature. One may make some allowance for the fact that the glass is partly dissolved in the course of analysis, for with many single determinations it makes no practical difference, but the patience of the analyst is sorely tried when an important determination is ruined by a beaker cracking on heating on a water-bath or hot plate.

In order to make a comparison of different kinds of chemical glassware the following samples were secured:

No. 2009. Flasks, of Kavalier Bohemian glass.

No. 2010. Beakers same as 2009. Kavalier's glass bears no trade mark.

No. 2011. Flasks of Weber's resistance glass, also known as Greiner and Friedrichs' resistance glass. Trade mark R.

No. 2012. Beakers same as 2011.

No. 2013. Flasks of Wiener Normal glass. Trade mark, "Wiener Normal Geräthe Glas."

No. 2014. Beakers same as 2013.

No. 2019. Beakers, Thüringen glass. No distinctive mark.

No. 2020. Beakers, flasks and Erlenmeyer flasks, Jena glass. Trade mark "Schott and Gen. Jena."

No. 2021. Beakers of "Nonsol" glass. Trade mark "Nonsol W. T. Co."

No. 2022. Beakers, flasks and Erlenmeyer flasks. Laboratory glassware, American. Makers' name on pasted label, but no permanent mark.

No. 2023. Beakers, Bohemian Normal glass from an American dealer. Paper label, but no permanent mark.

No. 2041. Beakers. Resistance glass of Vereinigte Fabriken für Laboratoriumsbedarf. No distinguishing mark.

No. 2042. Flasks. Same as No. 2041.

No. 2043. Beakers. F. Z. resistance glass. Trade mark "FZ."

No. 2044. Flasks same as No. 2043.

No. 2057. Bohemian glass beakers from an American dealer.

While it is well known that no great amount of information can be had from an analysis of glass, analyses were made of beakers of all the different kinds of glass. In most cases this analysis was simply a silicate analysis, using well-known methods. The precautions necessary have been very thoroughly discussed by Hillebrand.[1]

[1] Bulletin No. 176 of the United States Geological Survey.

The determination of boron presents some difficulty. The most satisfactory method is the combination of Gooch and Thomson methods used by Sargent in the determination of boron in tourmaline.[1] The use of mannite in the titration is to be preferred to glycerol, which Sargent used.

TESTS APPLIED.

A. Preliminary Treatment.—All samples before testing are carefully washed with pure water, filled with pure water and allowed to stand at a temperature of 20° to 25° C. for twenty-four hours, then rinsed with pure water and dried.

B. Mechanical Tests.—(1) (Applies only to beakers.) Fill beaker one-quarter full with a 10 per cent. solution of common salt, place on steam table and evaporate to complete dryness. Dissolve residue in water and repeat evaporation. This process is repeated four times, the beaker being finally left on steam table for six hours after it has become dry. After each evaporation careful examination is made for minute cracks.

(2) (When possible, use a beaker or flask of from 400 to 600 cc. capacity.) Fill half-full with water at 20 ° C. Place on a platinum triangle and heat with the direct flame of a Bunsen burner. The flame should be 12 cm. high, and top of burner 8 cm. below the bottom of the beaker.

(3) Pour boiling water into the beaker or flask at 20° C.

(4) Boil water in beaker or flask, empty and plunge into water at 20° C.

C. Solubility Tests.—(5) Carefully dry and weigh the vessel. Add 100 cc. of a 2 per cent. solution of sodium carbonate, cover and heat to boiling on a hot plate and boil twenty minutes, empty, wash with water, hydrochloric acid and again with water, dry and weigh. In testing beakers, but not flasks, the sodium carbonate solution is returned to the beaker and evaporated uncovered on the steam table to dryness, washed as before and weighed.

(6) Same as (5) except that a 2 per cent. solution of potassium hydroxide is used instead of the sodium carbonate.

(7) Same as (5), except that a 4 per cent. solution of ammonium carbonate is used.

(8) Place 100 cc. of neutral water in the vessels, cover with platinum dishes and keep on steam table for forty-eight hours, cool

[1] This Journal, **21**, 858.

and again make up to 150 cc. with neutral water, and take 100 cc. of this for titration. Place this 100 cc. in a stoppered bottle and add 20 cc. of an ethereal solution of iodoeosin (0.002 gram to 1000 cc.). On shaking, if any alkali is in the water it turns pink and this color is discharged by adding dilute acid. A N/50 sulphuric acid is used.[1]

(9) Fill vessels with the purest water that can be obtained, allow to stand at a temperature of 20° to 25° C. for twenty-four hours and determine the electrical conductivity. The conductivity measurements were made by Dr. Buckingham of the Bureau of Soils.

Of these tests the first is the only one that is new; it was suggested by Mr. L. S. Munson who had used it for several years before this work was taken up.

Table I shows the results of analyses of the different kinds of glass. As was to be expected, no very great amount of information can be gotten from this table, but it is of interest to note that we may divide the glasses into two distinct groups, Nos. 2010, 2019, 2022, 2023, 2041 and 2057 being alkali lime silicates, while Nos. 2012, 2014, 2020, 2021 and 2043 are borosilicates that have part of the lime replaced by zinc. It is also of interest that all of the borosilicate glasses may be distinguished by a permanent trade mark, and that these are the only glasses, so far as the writer has been able to learn, that are so distinguished.

Table II shows the results of the tests applied. Nos. 2020, 2021, 2012, 2043, 2014 and 2010 stood test No. 1. No. 2022 failed on the fourth evaporation in this test, No. 2041 on the third evaporation, and Nos. 2019, 2023 and 2057 failed on the first evaporation. It is interesting to note that of the six samples that stood this test five were the five trade-marked borosilicate glasses, the sixth sample being Kavalier's Bohemian glass.

Nos. 2020, 2021, 2012, 2043, 2014 and 2010 stood test No. 2. No. 2041 failed badly, and occasional samples of Nos. 2019, 2022, 2023 and 2057, failed. This test is not as useful as test No. 1. Where a very large number of samples are handled it is found that even with the most resistant glass occasional pieces will fail, while the greater number will stand; but with test No. 1 we have not ob-

[1] Mylius and Foerster: "Ueber die Bestimmung kleiner Mengen von Alkali und die Erkennung der Neutralitat des Wassers," *Ber.*, **24**, 1482.

TABLE I.—ANALYSES OF GLASSES EXAMINED.

Serial No.	SiO_2.	B_2O_3.	As_2O_5.	$(AlFe)_2O_3$.	ZnO.	MnO.	CaO.	MgO.	K_2O	Na_2O.	$M'_2O:M''O:\{\frac{B_2O_3}{SiO_2}\}$
2010	76.02			0.64		Trace	7.38	0.30	7.72	7.60	1.49 : 1 : 9.04
2012	68.00	5.53	0.24	2.32	2.40	0.14	4.80	5.04	1.82	10.17	0.75 : 1 : 5.01
2014	74.00	2.15		0.66	0.24	0.01	7.76	0.16	5.51	9.69	1.48 : 1 : 8.71
2019	74.36			0.90		Trace	9.40	0.16	0.14	14.83	1.41 : 1 : 7.24
2020	66.74	7.88		2.77	8.28	0.65	0.28	4.50	0.08	8.99	0.56 : 1 : 4.73
2021	65.04	6.23		3.78	8.88	0.04	1.75	1.44	0.08	12.72	1.15 : 1 : 6.55
2022	68.09			2.08		1.12	5.90	3.82	6.49	12.32	1.24 : 1 : 5.25
2023	73.80			1.00		1.04	7.88	0.08	7.67	8.59	1.38 : 1 : 7.38
2041	77.48			0.66		Trace	4.86	0.20	7.52	9.14	2.43 : 1 : 13.79
2043	68.96	6.02		0.70	8.65	0.11	0.26	5.05	3.64	6.71	0.62 : 1 : 5.25
2057	71.44			2.00		1.12	8.10	0.89	2.73	13.91	1.40 : 1 : 6.54

TABLE II.—RESULTS OF TESTS APPLIED.

Serial No.		Test 1.	Test 2.	Test 3.	Test 4.	Test 5. Loss in milligrams. A.	Test 5. Loss in milligrams. B.	Test 6. Loss in milligrams. A.	Test 6. Loss in milligrams. B.	Test 7. Loss in milligrams. A.	Test 7. Loss in milligrams. B.	Test 8. cc. N/50 H_2SO_4.	Test 9.
2009	Flask	.....	Good	Good	Good	11.0	....	7.8	....	0.8	...	0.85	300
2010	Beaker	Good	Good	Good	Good	11.2	20.4	12.2	18.6	0.8	1.8	0.20	298
2011	Flask	.....	Good	Good	Good	8.4	....	8.6	....	0.0	...	0.35	291
2012	Beaker	Good	Good	Good	Good	5.5	6.7	9.2	17.0	0.0	1.2	0.18	288
2013	Flask	.....	Good	Good	Good	15.0	....	8.8	....	1.4	...	0.90	299
2014	Beaker	Good	Good	Good	Good	11.8	20.9	18.3	24.7	1.4	3.6	0.20	295
2019	Beaker	Bad	Fair	Good	Good	7.0	22.2	10.8	17.0	1.0	2.6	0.09	295
2020	Beaker	Good	Good	Good	Good	3.8	4.4	16.4	26.4	1.2	2.4	0.10	294
2020	Flask	Good	Good	Good	Good	4.6	....	....	....	...	...	0.24	...
2021	Beaker	Good	Good	Good	Good	4.8	6.0	17.8	23.4	0.8	2.0	0.23	296
2022	Beaker	Bad	Fair	Good	Good	12.2	24.2	15.6	22.8	0.6	3.2	0.63	298
2022	Flask	.....	.....	.....	.....	72.0	....	....	....	...	...	5.08	...
2023	Beaker	Bad	Fair	Good	Good	12.4	24.0	10.2	16.6	0.6	1.8	0.22	337
2041	Beaker	Bad	Bad	Good	Good	10.0	21.0	9.17	17.0	1.9	1.9	0.65	...
2042	Flask	.....	Good	Good	Good	14.2	....	5.4	....	0.8	...	3.07	...
2043	Beaker	Good	Good	Good	Good	5.4	5.6	9.6	16.5	2.6	3.3	0.00	...
2044	Flask	.....	Good	Good	Good	8.2	....	6.6	....	2.8	...	0.39	...
2057	Beaker	Bad	Fair	Good	Good	....	....	....	....	...	...	0.17	...

served that any samples of the best glasses fail, and nearly all of the poorer grades fail in the first four evaporations.

Nothing can be learned from tests Nos. 3 and 4, as all the samples examined stood these tests.

In examining the results of the solubility tests one observes that there is in some cases a great difference between the solubilities of beakers and flasks of the same kind of glass, and as we had beakers of each kind and flasks of only a part of the samples, it is better in comparing the different kinds of glass to confine our attention for the present to the results on the beakers. In tests Nos. 5, 6 and 7 the columns marked A give the losses in milligrams after boiling with the solvent for twenty minutes, and columns marked B give the total losses after evaporating to dryness on the water-bath. Owing to the different shapes of beakers and consequent unequal evaporation and unequal changes in concentration, the losses on boiling for twenty minutes are much more variable than those by evaporating to dryness on the steam table. If we examine the results of test No. 5, column B, we see that we can divide the samples into two groups differing very much in solubility; the least soluble group Nos. 2020, 2043, 2021 and 2012 are all borosilicate glasses containing considerable zinc. Of the more soluble group No. 2014 is the only zinc borosilicate, and this glass contains much less zinc and boric acid than the other trade-mark glasses.

In test No. 6 we do not find the marked difference in solubility that was shown in test No. 5. Three of the borosilicate glasses, Nos. 2021, 2014 and 2020, are the most soluble, but the other two, Nos. 2043 and 2012, are among the least soluble. This test agrees with the results of Glinzer,[1] and of other observers who have pointed out that Jena glass is less soluble in carbonated alkalies and more soluble in hydrated alkalies than Bohemian glass. One would expect that the other borosilicate glasses would show the same peculiarity, but Nos. 2043 and 2012 seem to be remarkable in being slightly attacked by both carbonated and hydrated alkali.

Test No. 7 shows very little except that fixed alkalies have more effect on glass than ammonia. The amounts dissolved are in all cases so small that comparisons between the different samples are of very little value.

Test No. 8 is an important one, and while it cannot be taken

[1] *Z. angew. Chem.*, 1894, p. 743.

alone as a means of judging a glass, if taken in connection with test No. 1, can give one an excellent idea of the relative merits of different glasses. If we consider simply the beakers here, we see that all of those that required more than 0.4 cc. N/50 sulphuric acid were proved to be very poor glass by the other tests.

Test No. 9 was disappointing, an inspection of the results showing little difference between good and bad glass. The figures given are merely comparative, as the capacity of the cell used was not determined. The water used had a specific conductivity of 6.5×10^{-6} at 19°. While it is possible that somewhat better results may be gotten by using purer water, there appears to be no advantage in using this test, since test No. 8 gives us the necessary information as to solubility in water.

An examination of the results on flasks and a comparison of the results on the corresponding beakers shows the rather peculiar fact that a glass in the form of beakers seems to be more resistant to reagents than the same glass in the form of flasks. The writer cannot attempt to explain this peculiarity, but it is probably due to some difference in the annealing of the different forms of apparatus.

Some tests were made on the action of acids on glass, but the results only confirmed the conclusions of other investigators that glasses at all suitable for chemical work are much less attacked by acids than by alkalies or even water alone, consequently the tests with acid were soon abandoned.

One of the most prolific writers on the testing of chemical glassware has been Foerster, and it may be instructive to note in Table III the results of one of his investigations. This table is compiled from tables given in Foerster's article entitled "Vergleichende Prüfung einiger Glassosten hinsichtlich ihres Chemischen Verhaltens."[1] This table, among other things, shows that while the amount of alkali dissolved in hot water does not show the total matter dissolved by the water, yet it does show that alkali gives a very fair means of judging the relative solubility of the glass, and as in good glass the total matter dissolved is very small, its determination by loss of weight would be far from exact. Unfortunately, we can not take Foerster's determinations, which were published over eleven years ago, as necessarily bearing on glasses on the market at this time. Nos. 1, 2 and 10 are Jena glass, but a comparison of these analyses with those given in Table

[1] *Z. anal. Chem.*, **33**, 381.

TABLE III.—ANALYSES AND TESTS FROM FOERSTER'S WORK.

Number of glass.	K_2O.	Na_2O.	CaO.	ZnO.	MnO.	$(AlFe)_2O_3$.	SiO_2.	B_2O_3.	$R'_2O:R''O:SiO_2$.	Number of alkali molecules in 100 molecules.	Alkali given up to water expressed in thousandths of a milligram of Na_2O.	
											In eight days at 20°.	In three hours at 80°.
1....	....	11.0	....	....	0.05	5.0	71.95	12.0	.... :	10.8	2.5	2.7
2....	....	9.8	7.0	5.0	0.3	3.5	74.4	....	0.84 : 1 : 6.59	10.0	2.1	6.3
3....	5.8	7.6	10.4	....	....	0.3	75.9	....	0.99 : 1 : 6.81	11.2	10.7	28.4
4....	6.6	6.7	9.5	....	....	0.6	76.6	....	1.05 : 1 : 7.52	11.0	8.9	28.2
5....	6.2	6.4	10.0	....	0.2	0.4	76.8	....	0.95 : 1 : 7.16	10.4	13.1	26.8
6....	7.0	8.3	8.1	....	....	0.3	76.3	....	1.44 : 1 : 8.80	12.7	14.0	56.0
7....	11.8	4.9	7.6	....	0.1	0.5	75.1	....	1.50 : 1 : 9.24	12.8	14.5	45.0
8....	4.3	10.0	7.8	....	....	0.3	77.6	....	1.48 : 1 : 9.28	12.6	14.9	50.0
9....	4.6	10.1	7.7	....	....	0.4	77.2	....	1.54 : 1 : 9.36	13.0	17.8	66.0
10....	....	14.0	7.0	7.0	....	2.5	67.5	2.0	1.06 : 1 : 5.41	14.0	16.6	65.0
11....	0.6	14.3	11.2	....	0.4	2.9	70.6	....	1.18 : 1 : 5.88	14.6	27.0	98.0
12....	14.0	1.0	5.8	....	0.1	0.2	78.9	....	1.59 : 1 : 12.7	10.4	....	....
13....	1.8	12.9	11.0	....	....	1.3	73.0	....	1.16 : 1 : 6.20	13.8	....	....
14....	....	....	....	....	....	...	....	....	.... :	....	....	....
15....	9.7	9.0	6.8	....	Trace	0.4	74.1	....	2.04 : 1 : 10.17	15.4	32.0	217.0
16....	6.7	13.7	7.2	....	0.3	3.2	68.9	....	2.27 : 1 : 8.91	18.6	77.0	654.0
17....	12.7	....	....	PbO 30.0	....	...	57.3	....	1.00 : 1 : 7.10	11.0	74.0	350.0

TABLE III.—ANALYSES AND TESTS FROM FOERSTER'S WORK (*Continued*).

Number of glass.	Ratio of alkali given up to cold and hot water.	Loss in weight on three hours' treatment at 100° with 2 N alkali expressed in milligrams.		By treatment at 190° for four hours with water was dissolved in milligrams.			Number of molecules of silicic acid dissolved in water at 190° to each molecule of alkali dissolved.	Description of samples.
		Sodium hydrate.	Sodium carbonate.	Total.	Alkali.	Na_2O corresponding to the dissolved alkali.		
1....	1.1	67.3	23.5	23.7	3.5	3.5	6.0	Lime-free sodium borosilicate.
2....	3.0	39.7	17.6	....	....	....	....	Zinc lime glass containing aluminum, poor in sodium.
3....	2.65	35.4	....	....	....	....	....	Glass rich in lime, poor in alkali.
4....	3.17	37.5	59.5	17.2	5.6	4.6	2.65	Glass rich in lime, poor in alkali.
5....	2.05	....	....	....	....	....	....	Glass rich in lime, poor in alkali.
6....	4.00	39.8	76.9	....	....	....	....	Good lime alkali glass.
7....	3.10	37.7	79.2	51.3	15.4	11.1	3.35	Good lime alkali glass.
8....	3.40	38.5	73.0	....	....	....	....	Good lime alkali glass.
9....	3.72	42.4	79.4	67.0	16.4	14.7	3.57	Good lime alkali glass.
10....	3.91	46.5	23.0	34.0	6.4	6.4	4.42	Lime soda glass containing zinc oxide and aluminum.
11....	3.63	31.3	40.7	?	7.3	7.3	....	Lime-rich soda glass containing aluminum.
12....	....	....	....	63.0	16.2	10.7	4.5	Good potash glass, poor in lime.
13....	....	....	....	37.0	8.3	8.3	3.6	Lime-rich soda glass.
14....	....	....	....	87.0	....	29.0	....	
15....	6.78	....	....	....	....	....	....	Alkali-rich glass.
16....	8.5	46.0	45.0	126.0	61.0	52.0	1.3	Alkali-rich glass containing aluminum.
17....	4.73	58.0	51.0	....	....	....	....	Lead crystal glass.

I shows that none of them are the same as the Jena glass on the American market.

Nos. 3, 4 and 5 of Table III are said to be the glasses used by Stas. It is seen that these are good glasses and they approach the "normal" formula, the ratio $R_2O : R^{II}O : SiO_2$ approaching that of 1 : 1 : 6.

That this "normal" formula of a glass does not give us any guarantee that the glass is of good quality is shown by an inspection of the analyses and tests of samples Nos. 2010, 2022 and 2057. Nos. 2022 and 2057 have a ratio approaching much more nearly the normal ratio than No. 2010, and yet these two glasses are very poor glasses and No. 2010 is a good one.

In general, the conclusion to be drawn from this investigation is that the trade-mark glasses are zinc borosilicate glasses. That of these the Wiener Normal glass is the least resistant to reagents and the properties more nearly resemble the alkali lime silicate glasses. That of the other trade-mark glasses there is so very little difference in quality that the choice may be reduced to a simple consideration of price. That the alkali lime silicate glasses found on the American market are usually of very poor quality. This inferior quality is very probably due to the fact that the consumer has no means of identifying the different makes. He may order Kavalier's glass and may be furnished glass that was made by an entirely different factory. One thing that we need is that all makers of chemical glassware mark their products with some distinct and permanent trade mark, and when that is done we can learn which trade marks mean good glass and know that we are getting what we order. This has been done by the makers of the borosilicate glass, but there is undoubtedly a demand for good glass of the Bohemian type.

The writer, in conclusion, wishes to express his obligations to Mr. L. S. Munson for many suggestions in connection with this work.

CONTRACTS LABORATORY, BUREAU OF CHEMISTRY,
WASHINGTON, D. C., April 14, 1905.