[CONTRIBUTION FROM THE LABORATORY OF THE CORNING GLASS WORKS]

Extraction and Analysis of Gases from Glass[1]

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Introduction

In the course of a study of gases in glass there arose the problem of working out an apparatus for extracting and quantitatively analyzing the gases from molten glass. A fairly successful system has been developed and thoroughly tested in use. Since the procedures differ considerably from any previously described and involve some points of general interest in high temperature technique it was thought worth while to publish a brief description of them. To illustrate the behavior of the apparatus it was also decided to include the results of some test analyses and of some determinations on typical glasses that are of general interest.

Various other investigators have studied the gases in glass, but most of them have confined their observations to temperatures below the softening point. At these lower temperatures the quantity and nature of the gas is different, as is also the procedure necessary for extraction, so it is beyond the scope of this paper to discuss these investigations. The earliest work at high temperatures was that of E. S. Shepard mentioned in an article by Allen and Zies.[2] This was followed by the more extensive work of Washburn, Footitt and Bunting.[3] Both of these investigations failed to provide for the detection and estimation of water vapor, which is almost always an important constituent of gases coming from glass. A more complete investigation has been reported by Salmang and Becker.[4] The results of the present work are in general agreement with theirs, although the analytical and extraction methods differ considerably in the two cases.

Some earlier experiments by the author[5] indicated that water, carbon dioxide, sulfur dioxide and oxygen were the principal gases to be expected. It was also apparent that it would be an advantage from the viewpoint of extraction to keep the size of the glass samples down to a gram or so. This meant dealing with gas samples averaging around 0.5 cc. in volume but falling as low as 0.01 cc. in special cases.

The apparatus divides itself naturally into two parts, the extraction apparatus and the analytical apparatus. The extraction is carried out by melting the glass in vacuum and pumping off the gases. The analysis is carried out at low pressure using physical methods of separation where possible.

Extraction Apparatus

The general problem in the extraction process is that of designing an apparatus which will be gas tight at 1400° in vacuum and which can be baked out so that it will not itself give off appreciable quantities of gas. Sillimanite has been found to be the material most nearly fulfilling these conditions.

Figure 1 shows a cross section of the apparatus. The outgassing takes place in the sillimanite (Champion 6060) tube (F). Fortunately this can be sealed directly to "Pyrex" brand chemical glass of which the whole apparatus is constructed, thus making it possible to eliminate all wax and greased joints. This porcelain to glass seal is easily made in diameters up to 1.3 cm. and is quite useful for vacuum technique at high temperatures. Sillimanite tubes up to 1.3 cm. diameter and 1.6 mm. wall will stand a full atmosphere at 1450° without appreciable collapse. A new tube is used in each determination.

The heating is done by means of a winding of 75 mil tantalum wire embedded in alundum. Tantalum has been found superior to molybdenum as its oxide is not volatile and the wire is more easily bent into form (when new). The heater (H) is surrounded by two concentric cylindrical shields (C_1) and (C_2) of tantalum or molybdenum to act as radiation reflectors. To protect the metals from oxidation the whole furnace system is enclosed in an evacuated glass tube (D). This serves the additional purpose of eliminating any possibility of gases getting into (F) and of cutting down heat loss from the furnace. The tube (D) has its own vacuum pump and there is no connection with the main vacuum system. The ground glass joint (J) is sealed with wax and the whole tube is surrounded by a water jacket (not shown). A sample tube (G) with magnetic plunger furnishes a means of introducing the sample which is in the form of short lengths of rod. This is done after the apparatus has been evacuated and baked out. The bake out is continued until tests show that the gas evolved is negligible compared to that expected from the glass. This normally requires about a thirty-minute

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[1] Presented at the New York Meeting of the American Chemical Society, April 22, 1935.

[2] E. T. Allen and E. G. Zies, *J. Am. Ceram. Soc.*, **1**, 739 (1918).

[3] Washburn, Footitt and Bunting, Univ. of Ill. Eng. Expt. Sta. Bull. 118 (1920).

[4] H. Salmang and A. Becker, *Glastech. Ber.*, **5**, 520 (1928); **6**, 625 (1929); **7**, 241 (1930).

[5] R. H. Dalton, *J. Am. Ceramic Soc.*, **16**, 425 (1933).

treatment at 50° above the temperature at which the glass is to be outgassed. The temperature is measured through the window (W) by means of an optical pyrometer and any temperature up to the melting point of sillimanite can be attained. The glass samples are usually outgassed at 1400°, however. The tube (L) leads to the pumps and the analytical apparatus. The pumping system consists of a two stage mercury vapor pump backed by an oil pump.

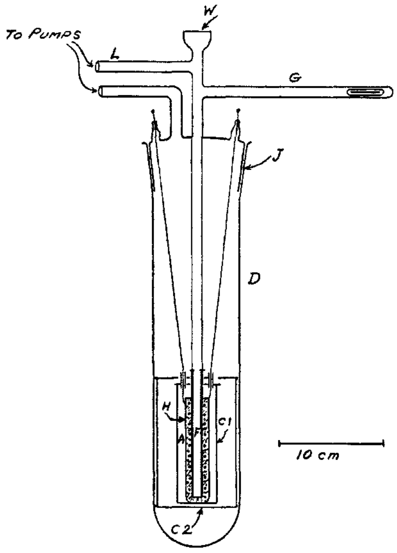

Fig. 1.—Outgassing furnace.

There is one serious source of error in this method of extraction which we have found no way to eliminate entirely. This error is due to the volatilization of oxides such as Na_2O, B_2O_3, etc., which condense in the tubing just above the furnace and reabsorb part of the gases before they reach the analytical apparatus. In view of this, coupled with the fact that the work is in a fairly new field where it is of greater interest to obtain approximate results on a number of glasses than very accurate results on a few, no attempt has been made to push the accuracy of the analytical part of the apparatus to the limit.

Analytical Apparatus

The analytical apparatus must provide means of pumping the gases from the furnace and of analyzing for water, carbon dioxide, sulfur dioxide and oxygen. It was desired also to provide for hydrogen and carbon monoxide in case these should be present. Nitrogen plus other inert, non-condensable gases could be determined together as a residue. The fact that the gas samples come from glass at 1400° simplifies the problem in that oxidizing and reducing gases cannot come off together. The procedure consists in general of freezing out the water, sulfur dioxide and carbon dioxide in the order named, then removing oxygen by hot copper and finally oxidizing carbon monoxide and hydrogen with copper oxide.

A brief mention will be made of an early form of the apparatus as it worked fairly well and had a great advantage in simplicity. This apparatus is shown diagrammatically in Fig. 2. The gas evolved from the molten sample enters the system through the special stopcock (S_1) which is in position to connect 1 and 2 and close off 3. The gases then pass through the trap (T) where water is frozen out by cooling with solid carbon dioxide and thence into the bulb (B). From here the gas can be pumped into the space between (S_1) and (S_2) by raising the mercury from the reservoir (R_2). In this way the bulb (B) acts as a form of Toepler pump, withdrawing the gas from the furnace and transferring it to the small volume above (S_2). The water that has been collected in (T) is determined by confining it between the points (AA) and measuring the pressure that develops when the trap and connecting tubes are completely immersed in boiling water. The volume between (AA) is accurately known and is such that the water vapor is always well below the saturation pressure at the temperature of the surrounding bath. The total volume of gas other than water is measured by letting the gas expand back into B, and measuring the pressure at one of the points of known volume (V_0–V_5). This measurement is in error, of course, by the ratio of the volume (S_1–S_2) to the total volume above (P), but this error can be made smaller than that from other sources.

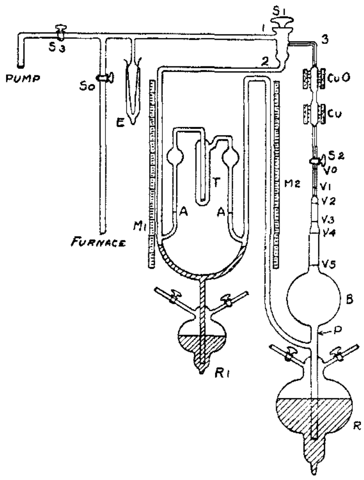

Fig. 2.—Analytical apparatus.

To determine the other gases the sample is recirculated through appropriate refrigerants and reagents as will be described in detail later in connection with final form of the apparatus.

This simple apparatus worked quite satisfactorily in most respects but in order to eliminate occasional trouble with leaking and plugging at the stopcock (S_2) it was decided to go over to a system in which there were no stopcocks. This would have the additional advantage of avoiding any contamination by vapors of stopcock grease. The method of determining water was simplified at the same time and the error due to the volume (S_1–S_2) was eliminated. The final form of the apparatus is shown in Fig. 3. In order to show things clearly the small parts have been drawn to a magnified scale so no indication of relative size is given by the diagram. Also the whole thing has been compressed vertically to save space.

The apparatus is best understood by tracing through the procedure, which is as follows. After the reading of the Pirani gage (E) indicates that a good vacuum has been obtained the mercury is raised in (H_1) and (H_3), thus cutting off the pumps and the reagent tubes. The glass sample is then added to the extraction furnace and the Toepler pump (B_1) is operated thus drawing the gas from the furnace through the trap (T) and compressing it into the gas buret (G) where the volume can be measured. The water vapor is removed from the gas as it passes through (T) which is cooled with solid carbon dioxide. When the major part of the gas has been extracted, which takes usually around half an hour, the furnace is closed off at (H_2) and the water is allowed to vaporize, filling the space between (H_1), (H_2), (H_3) and the trap in the capillary leading to (G). The volume of this space is known, and from the pressure reading on the Pirani gage which has been calibrated for water vapor, the quantity of water can be determined. The electrical circuit is that suggested by Campbell[6] in which the gage is in one arm of a Wheatstone bridge, the three other resistances of which have fixed values such that the bridge balances when the filament is around 100°. The bridge voltage necessary to obtain a balance is a measure of the gas pressure in (E).

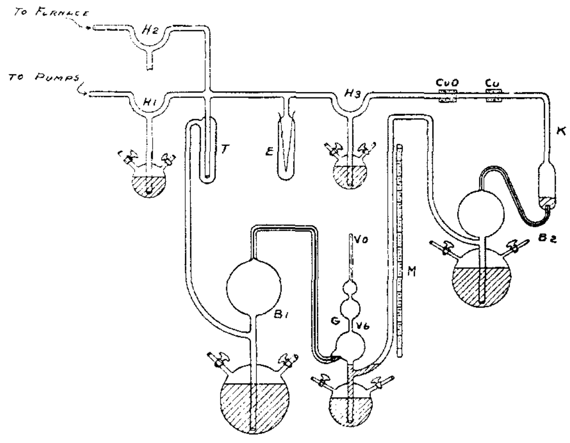

Fig. 3.—Analytical apparatus.

Using a gage with a filament of 28 cm. of 2 mil platinum wire, the voltage reading ran from 1 volt in vacuum to about 9 volts with a pressure of 4.59 mm. of water vapor. The voltmeter reading could be made to 0.01 volt. This method of determining water vapor has proved fairly satisfactory and is much easier and quicker than that described before. It has a disadvantage, however, in that there is sometimes a gradual drift in the gage reading, probably due to changes in the adsorbed gases on the filament surface. In this case it is necessary to wait until a steady value is reached before making the reading. The gage is immersed in a water-bath (not shown) maintained at an approximately constant temperature. After being determined, the water is removed from the apparatus by opening (H_1) to the pumps.

Sulfur dioxide is determined next by cooling (T) to −140° with a special bath and pumping the gas around with the Toepler pumps (B_2) and (B_1). The cut-off (H_1) is, of course, closed and (H_3) open. The cooling bath consists of petroleum ether in a heavy copper tube, the lower end of which terminates in a copper rod dipping in liquid air. The tube is wound around with a resistance heater. By properly balancing the cooling effect of the liquid air and heating effect of the current it is possible to hold the temperature of the bath within two or three degrees, which is close enough for our purpose. Temperature is measured with a small thermocouple immersed in the ether. The decrease of pressure in (G) when all the gas has been returned gives the sulfur dioxide content. If the Pirani gage were calibrated for this gas, it could also be determined in the same way as water.

For carbon dioxide the gases are circulated again as above except that the trap is cooled in liquid air. To be sure of the nature of the gas frozen out, the vapor pressure may be followed as the trap is allowed to warm up gradually. The vapor pressure of a gas is a fairly characteristic property and in a case like the present where only a few gases can conceivably be present it serves as a satisfactory identification.

Oxygen is determined by heating the tube containing metallic copper to around 350 or 400° and recirculating the gases. Before the gases are admitted, the reagent tube is given a good bake-out while open to the pumps. This is necessary to avoid errors due to gases given off by the hot glass or by the copper itself. As an additional precaution (T) may be immersed in liquid air, as most of the evolved gas is removed at that temperature. If only a small quantity of oxygen is expected the gas can be compressed over the reagents by closing (H_3) and filling the trap and tube (K) with mercury from (B_2). This accelerates the reaction.

For the measurement of carbon monoxide and hydrogen the gases are circulated over hot cupric oxide. The oxidation is quite slow in the case of carbon monoxide so the gas must be compressed as much as possible and left in contact with the cupric oxide for some time. In this case the previous outgassing of the reagent tubes must be particularly thorough as water vapor is the principal gas given off by the glass walls of the tube. Any water formed is collected in (T) by cooling with solid carbon dioxide and measured as before. It could also be obtained by the drop in pressure in the gas buret provided, as in our case, oxidizing and reducing gases cannot be present together. The carbon dioxide is measured as was that in the original sample.

Any inert, non-condensable gas which remains in (G) after the analysis would probably be nitrogen or one of the inert gases. In the samples we have run which came from glass there has never been any appreciable residue at this point.

The complete analysis of a gas sample requires about half a day. This does not include the time for outgassing the glass sample.

Analytical Results

The results of some test analyses are given in Tables I and II. Table I gives the results with the first form of the apparatus and Table II with the present one. With the latter, the errors vary from 0.5% or less in samples of 1 cc. or so up to several per cent. in small samples.

Since the apparatus was completed gas analyses have been run on several hundred glass samples. All samples except those that had been

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(6) Campbell, *Proc. Phys. Soc.* (London), **33**, 287 (1921).

previously outgassed gave off appreciable quantities of gas. On the average it may be said that the volume of gas at standard conditions is at least as great as the volume of the glass sample. Table III gives some typical results obtained by three different analysts. A separate glass sample was used in each check analysis. The symbol R stands for residue of inert gas.

TABLE I

TEST ANALYSIS RESULTS

Sample, cc.		Composition, % Synthetic	Detd.		Synthetic	Detd.
1.47	SO_2,	48	48	CO_2,	52	51
1.52	SO_2,	40	41	CO_2,	60	59
2.79	O_2,	21	20	N_2, etc.	79	80
1.82	O_2,	21	21	N_2, etc.	79	79

0.39 cc. CO; found, 0.38 cc. 1.20 cc. H_2O; found, 1.22 cc.

TABLE II

TEST ANALYSIS RESULTS

Sample, cc.		Composition, % Synthetic	Detd.
0.0284	O_2,	21.0	21.8
	N_2, etc.	79.0	78.2
.114	CO_2,	37.7	36.8
	SO_2,	62.3	63.2
.526	H_2,	0.526 cc.	0.523 cc.
.890	CO_2,	20.2	20.3
	O_2,	16.8	16.8
	N_2, etc.,	63.2	63.0
1.006	H_2O,	71.0	71.1
	O_2,	6.1	6.3
	N_2,	22.9	22.6

TABLE III

No.	Glass type	Gas, cc.	Percentage composition of gases H_2O		SO_2		CO_2		O_2		R	
I	Barium (optical)	0.71	24	22	..	..	40	37	36	41	0.1	0.1
II	Soda-lime (milk bottle)	.93	51	51	33	34	3	3	12	11	0.1	0.1
III	Borosilicate (heat resistant)	.40	91	92	..	..	5.5	4.5	3.5	3.5	..	..
IV	Soda-lime (bulb)	.90	44	44	35	36	4.5	7	16	13	..	..
V	Borosilicate (heat resistant)	.36	92	89	0.3	0.3	3	4	5	7	..	..
VI	Borosilicate (bulb)	.74	94	94		2.5	3		3	3.5	..	..
VII	Lead (sign tubing)	.70	33	39		8	7		59	54	..	..
VIII	Soda-lime (expt.)	1.41	28	28		10	8		62	64	..	..
IX	Borosilicate (heat resistant)	0.44	93	93		2	4		5	3	..	..

As may be seen from the table, it is impossible to check successive samples as closely as would be anticipated from the results of test analyses. This is due to difficulties in the extraction apparatus, previously mentioned, the principal of which is reabsorption of the gases by materials that are volatilized from the glass and condense in the cool upper section of the furnace tube. Sodium oxide probably causes the most trouble. Ways have been found to diminish this effect, but so far no way has been found to eliminate it. The best system is to clean the furnace tube thoroughly after each run, use a new crucible, and pump the gases away from the furnace as rapidly as possible.

The table gives, in addition to the composition of the gas, the general type of the glass and the volume of gas at standard conditions obtained from a gram of sample. The latter is many times that obtained at low temperatures where the glass is still solid. All glasses examined contained water and this was usually the most abundant constituent. Carbon dioxide is also nearly always present though often only in small quantities. Sample No. 1 contained a large volume of carbon dioxide due to the basic character of barium oxide. Glasses which contain sodium sulfate give off sulfur dioxide, and those containing higher oxides of arsenic or iron give off oxygen. The gases carbon monoxide and hydrogen were rarely found present, and there was never an appreciable residue of inert gas. Glasses VI to IX may contain some sulfur dioxide but no test was made for this gas so the figure given represents the sum of sulfur dioxide and carbon dioxide. Sample No. VIII was an experimental glass of unusually high arsenic content.

In conclusion the author wishes to express his thanks to Messrs. W. C. Taylor and H. P. Hood for supervising the work and to A. Jacoby for valuable assistance in carrying out the experiments.

Summary

An apparatus is described for collecting and analyzing the gases evolved by glass when heated in vacuum. The apparatus takes samples of from 1 cc. to 0.01 cc. and analyzes for H_2O, CO_2, SO_2, O_2, H_2, CO and N_2, etc. (by difference). Results of test analyses and results with some typical glasses are given.

CORNING, N. Y. RECEIVED JULY 1, 1935