[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORY.]

EFFECTS OF HEAT ON CHEMICAL GLASSWARE.

BY R. G. SHERWOOD.

Received August 12, 1918.

Introduction.

When a glass vessel, designed for vacuum purposes, is being exhausted to a high degree of vacuum it is common practice to simultaneously subject it for some time to a heat treatment at temperatures ranging between 200 and 400° C. This heating greatly assists exhaustion by accelerating the removal of all adsorbed gases and vapors from the inner surface of the vessel. As a result of a series of experiments the writer concludes that the comparatively large quantities of these gaseous products obtained upon heating the walls of an exhausted vessel cannot be ascribed entirely to surface adsorption. The method used in a study of this problem with a few of the results obtained and conclusions drawn may be of some interest.

Apparatus.

The assembled apparatus, with the exception of the mercury diffusion pump, is shown diagrammatically in Fig. 1. The system is constructed entirely of Corning G–702–P glass which has been found to be especially suitable for all such constructions. Pressure determinations within the system are made by means of a mercury U-tube manometer, M. In order to eliminate all capillary effects the upper portions of the manometer are made of large tubing, 3 or 4 cm. in diameter. A micrometer microscope focussed upon one of the mercury surfaces furnishes a very satisfactory means for measuring the differences in level of the mercury. With clean, dry mercury a change in level of 0.01 mm. can readily be measured. In order to be assured of dry mercury, free from any entrapped air, filling of the manometer is accomplished by means of the device shown in the figure. After a fair degree of vacuum has been attained within the system the mercury contained in the reservoir is first raised and lowered several times without, however, allowing it to flow over into the manometer; by gently heating with a flame during

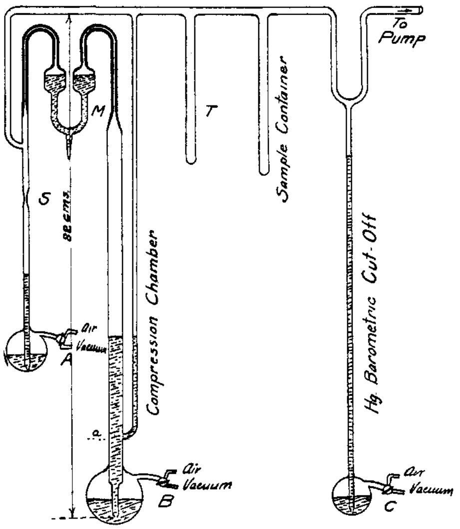

Fig 1.

the process of raising and lowering, the mercury is readily freed from all moisture or occluded air and can then be allowed to flow over into the manometer to any desired height. After filling has been accomplished the mercury reservoir is removed by being sealed off from the system at the constriction S. If at any time it becomes necessary to remove the mercury from the manometer this can easily be done by simply breaking off the end of the small projecting tubing shown in the figure. The compression chamber functions in the same way as does that in the ordinary McLeod gauge. In the particular piece of apparatus used by the writer the total volume of the compression chamber was 204 cc. and the smallest volume to which the gas contained therein could be compressed was 2.96 cc. With this ratio it is obvious that pressures as low as 0.001 mm. of mercury can be measured with good precision. One advantage this form of construction possesses is that a wide choice of volume ratios is possible, which is of particular advantage where vapors are present, since a ratio can always be so chosen that there will be produced not more than a few tenths of a millimeter difference in level in the manometer arms. For instance, the saturated vapor pressure of water at room temperature is approximately 20 mm.; consequently a difference in level of even one or two millimeters would not be sufficient to cause any appreciable deviation from Boyle's law for water vapor. With a system of considerable capacity therefore comparatively large quantities of water vapor can be measured with some degree of accuracy, especially where errors as large as 10% on a single measurement are permissible as, for instance, in the work herein to be described. Calibration of the manometer is perhaps most readily accomplished by comparison with a McLeod gauge.

Method.

If "L" represents the change in level in millimeters of the mercury surface in one of the manometer arms when compression has been made, it can be shown that the pressure P within the system is given by the relation $P = 2L/R - 1$ (1), R being the ratio value chosen. Whence it follows directly from Equation 1 that the quantity of gas in the system expressed in cubic millimeters is given by the expression $Q = 2LV/0.76\ (R - 1)$ (2), where V is the volume of the system in cc. If a McLeod gauge is used to calibrate the compression manometer, the value of $(R - 1)$ can be obtained from Equation 1 and as a working formula we then have $Q = KL$ (3), where $K = 2V/0.76(R - 1)$. The value of K can, of course, be determined for a number of settings along the compression chamber.

After a sample has been placed in the container shown in Fig. 1 the latter is sealed, not waxed, on to the system. After the system has been exhausted to 10^{-3} or 10^{-4} mm. of mercury pressure, the forward part is then completely cut off from the pump by means of the barometric mercury "cut-off" shown. In this way all vapors and gases afterwards liberated from the sample will be confined within the portion of the system between the manometer and the "cut-off." Preliminary work has shown that the error introduced by adsorbed gases coming off the walls of the system, after one or two hours of pumping, is entirely negligible as compared to the actual quantities of gases and vapors dealt with during the test. Heat is applied to the sample container by means of a small, nichrome wound, tubular, electric heater, the temperature of which can be readily controlled. For the results appearing in this paper the form and dimensions chosen for the sample consisted of three coaxial, cylindrical tubes 15 cm. long with inside diameters of approximately 10, 8, and 6 mm., respectively, and having a wall thickness of about one mm. The sample container was about 30 cm. long with an inside diameter of about 15 mm. The total area of the glass thus exposed to a vacuum and receiving a heat treatment was approximately 350 sq. cm. For all the work appearing in this paper the container consisted of the same glass as that composing the system. Having a high softening point with a small expansion coefficient this glass is particularly well suited for use in a container. It will be shown later how a container which has once received an annealing treatment for a couple of hours at a definite high temperature, say for example 600°, will thereafter not introduce appreciable error into the results when samples of other glasses are being tested in it, provided the temperature applied is not raised beyond the annealing temperature to which the container had previously been subjected.

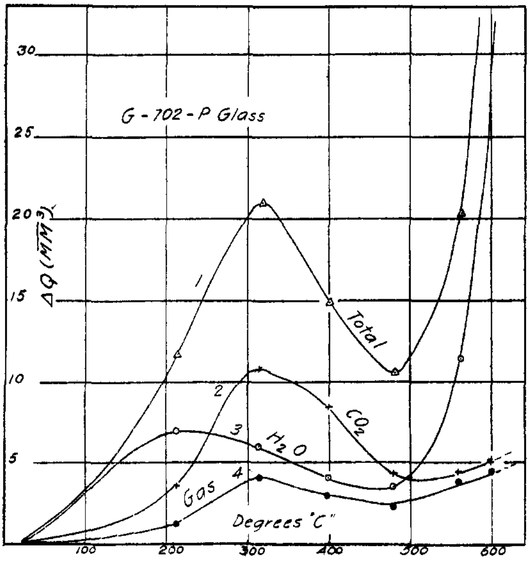

Fig. 2.

Results.

The data from which the curves shown in Fig. 2 were plotted were taken on Corning G–702–P glass. Curve 1 shows the relation existing between the total quantity of gaseous emission products driven off from the sample by the application of heat, and the temperatures at which the heat was applied to the sample. The sample in this experiment was subjected to a series of successive temperatures, the period of heating being chosen as 3 hours in each case. A partial separation of the evolution products was effected by the use of carbon dioxide snow and liquid air placed about tube T (Fig. 1). The carbon dioxide snow freezes out all water vapor into the tube T leaving behind the carbon dioxide and other gases not so condensed. On the other hand, liquid air removes both the water vapor and the carbon dioxide. From the above 3 sets of observations on the pressure, the evolution products are separated into 3 parts, *viz.*, water vapor, carbon dioxide and those products not removed by the application of either liquid air or carbon dioxide snow such for instance, as nitrogen, hydrogen, oxygen, carbon monoxide, etc. These latter collectively will be designated by the term "gas." There is no doubt that these latter are adsorbed to some extent by the walls of the tube T due to the great lowering in the temperature, but preliminary work has shown that dry air under similar conditions does not adsorb sufficiently to cause any appreciable error in the work; at any rate this adsorption is within the error introduced by the change in pressure within the system, due solely to the heating of the gas, which an approximate calculation has shown to be less than 5% at most. Attention is called to the relative characteristics of the four curves shown in Fig. 2. The logical interpretation to be given these results, it seems to the writer at least, is that in addition to the removal of the adsorbed products which takes place mostly between 100° and 300° there is also another kind of gaseous evolution consisting principally of carbon dioxide and water vapor. At the lower temperatures this latter evolution is not very pronounced, but for temperatures above 500° it becomes the chief effect. The very marked and rapid rise of the water vapor curve is very significant, suggesting that at temperatures above 500° the glass is in the process of forming new chemical equilibria. The curves in Fig. 3 are also of interest since they show the relative proportions of the above emission products given off at the dif-

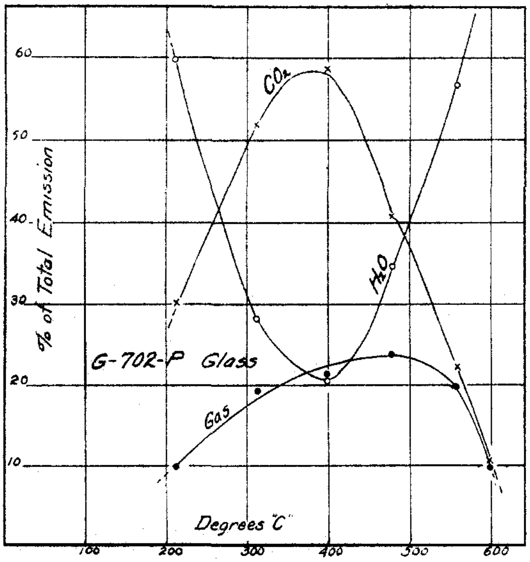

Fig. 3.

erent temperatures. The data for these curves were obtained from the curves given in Fig. 2.

The data for the curves shown in Fig. 4 were obtained by subjecting a sample of G–702–P glass to a series of successive temperature increments as in the preceding case except that heating periods of 24 hours instead of 3 hours were used. Curve 1 shows the percentage of total emission products still obtainable at the end of 3 hours of heating on the basis of the total emission which resulted from the 24-hour heating. For the higher temperatures, even after 24 hours of heating, the sample continues to give off gaseous products upon still further heating. In one instance this liberation was observed to take place even after 40 hours of heating, the temperature used being about 500°. The rapid and continuous rise in the above curve, within the temperature range 300° to 500°, clearly indicates an evolution quite different from what might be expected as the result of adsorbed products only; but on the other hand this might be readily expected on the assumption that the formation of new chemical equilibria is the cause of the phenomenon. Curve 2 in this same figure gives some idea concerning the rate of the evolution, and is obtained by plotting the slopes of the quantity-time curves taken for the successive baking temperatures above mentioned. In this connection it was observed that these, quantity *vs.* time curves, all rose rather steeply during the first part of the heating, then began to flatten out rapidly and after 5 or 6 hours all tended to become more or less linear. The slopes of the upper portions of these curves were accordingly taken as a rough measure of the evolution rates for the respective baking temperatures.

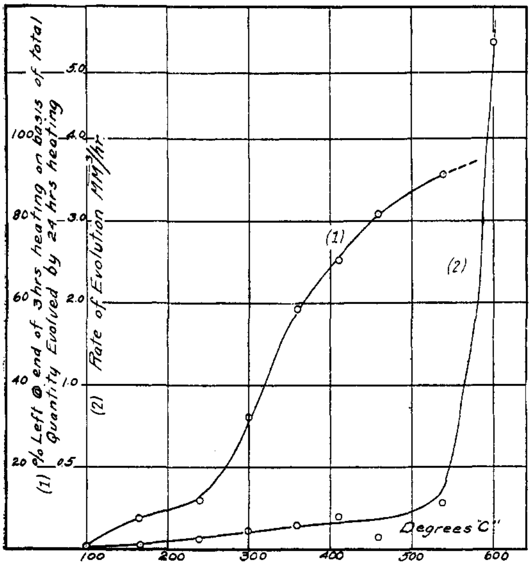

Fig. 4.

On the assumption that there is a chemical change in the glass taking place under the influence of the heat, it is logical to expect that this should also occur when glass is being heated at atmospheric pressure. The curves given in Figs. 5 and 6 bear on this point. Consider the curve in Fig. 5. In this case several samples of the same glass, all having the same dimensions and receiving the same vacuum heat treatment were given preliminary annealing treatment for the same time period but at different temperatures. The ordinates of the curve represent the total quantity of gaseous evolution products obtained from the particular sample whose preliminary annealing treatment is given by the corresponding abscissas. The temperature used in the vacuum heat treatment for all cases was 500° and the period of annealing was one hour. Time of exposure to room air after the annealing process proved to have little or no effect even after a period of several days had elapsed between the annealing and the sealing of the samples onto the system. If we assume that adsorption of gases and vapors upon glass is confined to a layer approximately one molecule deep, then for the area of the glass heated, this quantity would correspond roughly to about 10 cu. mm. In this connection the above curve is of some interest, since it apparently approaches an asymptote corresponding to a value not greatly different from the above value. The curves in Fig. 6 are also of interest in this connection. Each curve here shows the total emission from a particular sample which has previously been annealed for a two-hour period at the temperature designated upon the curve. The abscissas represent the temperatures of the successive vacuum heat treatments applied to the samples, the time of

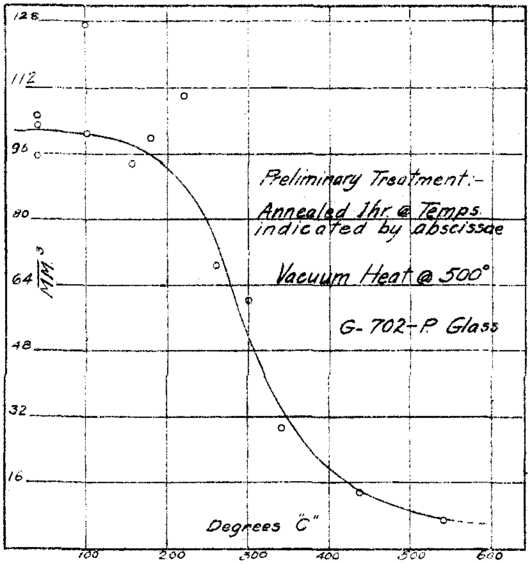

Fig. 5.

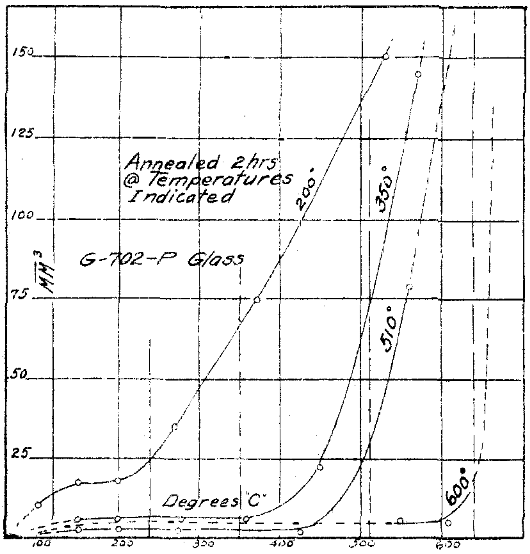

Fig. 6.

heating being about one hour. The ordinates give the integrated total of the emission products up to and including the temperature shown by the corresponding abscissas. It is seen from these results that practically nothing more than absorbed products are obtainable from the samples until after the previously annealing temperature has been passed; also as is seen from the horizontal portion of the curves the quantity of adsorbed products obtained is of the magnitude above stated, and that these products are readily and more or less completely removed at the lower temperatures. It is understood here, of course, that the discussion regarding adsorbed products refers only to adsorption which exists under good vacuum conditions and at room temperature. As the curves in Fig. 6 show, there occurs in every case a further marked evolution of gaseous products from the sample when it is being heated at a temperature greater than the annealing temperature to which it had previously been subjected.

From the results which have just been discussed, it is obvious why a container made of a hard, high-softening-point glass, which has once received an annealing treatment at say 600° for a couple of hours, can therefore be used as a container for samples of other glasses in a similar investigation and where the temperatures used are below 600°. The writer has taken some data on both soda and lead glasses, using a G–702–P glass container treated as described above. The error introduced into the results due to adsorbed products from the container would be unimportant since the quantity of evolution products in all cases are very large as compared to the quantity of gas or vapor introduced through adsorption. The results on these other glasses will be only partially incorporated in the present paper. In Fig. 7 there are 3 curves which correspond to Curve 1 of Fig. 2 for the G–702–P glass. Attention is directed to the relative position of the maximum and minimum points. It can be seen that the softer, lower-softening-point glasses lead and soda, show that decomposition becomes more pronounced at a lower temperature than in the case

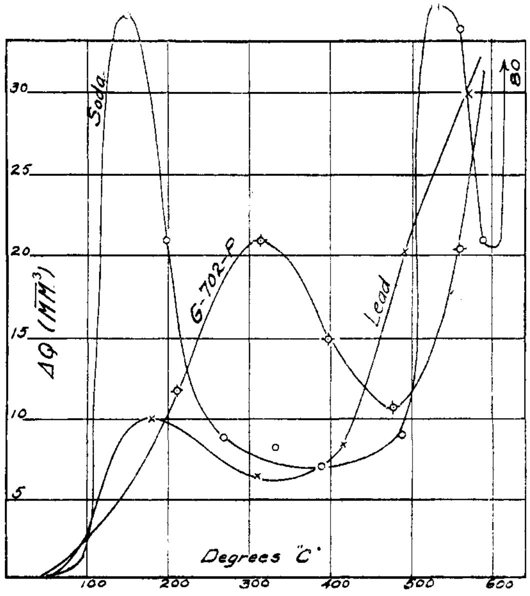

Fig. 7.

of the hard G–702–P glass. The curve for the soda glass is of particular interest since it possesses double maxima and minima. The water-vapor curve for this same glass shown in Fig. 8 possesses the same general characteristics as the total emission curve; also it shows that the water constituent is by far the most important one. In Fig. 9 is shown the same class of curves taken for the lead glass before mentioned. It is noticed that in the case of both lead and G–702–P glass the carbon-dioxide curves possess distinguishing characteristics not particularly marked in the case of the soda glass. Mr. H. M. Ryder, of this laboratory, has checked some of the writer's results on G–702–P glass using an entirely different method. He has, moreover, carried the analysis of the evolution products further and has found that the residual products, left after carbon dioxide and water vapor have been removed, are composed largely of carbon monoxide, hydrogen, and but a relatively small quantity of nitrogen.

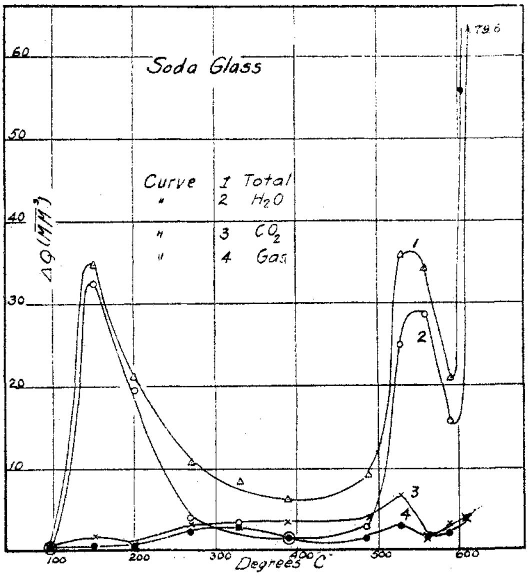

Fig. 8.

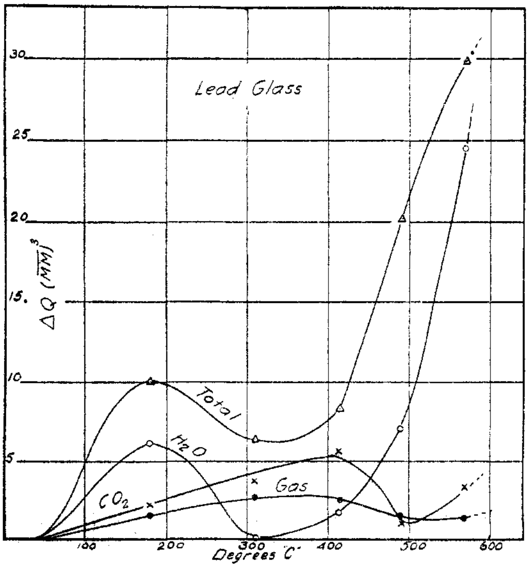

Fig. 9.

Summary.

1. When glass is heated there is evidence of two distinct kinds of gaseous evolution; that resulting from adsorbed products which are readily removable at temperatures below 300° and that resulting, in all probability, from a chemical decomposition of the glass itself. The latter effect becomes important

above 400° for the softer glasses tested and above 500° for the harder glass.

2. There is some evidence of a definite characteristic rate of gaseous evolution for each temperature to which the glass is subjected, increasing with the temperature and extending over a considerable period; observations on one sample at 500° showed a small continuous evolution even after 20 hours of heating.

3. Adsorption products are confined to quantities which are represented approximately by a layer of gas about one molecule deep and are removed with much greater rapidity at lower temperatures than the other products obtained due to the heating of the glass.

4. The most important of the gaseous evolution products obtained from glass under the influence of heat is water, which, as the temperature is raised to the softening point of the glass, constitutes almost the entire quantity of the evolution, but which at a lower temperature may be relatively unimportant.

[Contribution from the Chemical Laboratory of the University of North Carolina.]

ZIRCONYL BASIC CHROMATE.

By F. P. Venable and L. V. Giles.

Received August 26, 1918.

There are two references in the literature to compounds of zirconium and chromic acid. The first is by Weibull,[1] a mere note as to the formation of a precipitate on adding chromic acid to a solution of zirconium oxychloride without details as to its composition. The second is by Haber,[2] who reports that zirconium is easily precipitated by free chromic acid as a flocculent, orange-yellow precipitate, difficulty soluble in dilute acid. It is also precipitated by bichromates and chromates. Our experience with fairly strong solutions of the oxychloride and also of the basic sulfate shows that potassium chromate yields an immediate, heavy, flocculent, yellow precipitate, while the bichromate precipitates much more slowly and less thoroughly, and a strong solution of chromic acid causes no precipitation at all unless heated or, better still, after dilution and heating.

Haber obtained the compounds analyzed by him by using the bichromate and concluded from his analyses that the salt was basic, since the proportion of the zirconia was too high for the normal salt. Furthermore, his presumption was that chromium trioxide was partially removed by the washing with water, though it could not be entirely removed even by boiling with water. This presumption was based on results of analyses

---

[1] *Acta Univ. Lund.*, [II] 18, V 57 (1881–1882).

[2] *Monatsh. d. Chem.*, 18, 667 (1897).