

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.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

### ZIRCONYL BASIC CHROMATE.

By F. P. VENABLE AND L. V. GILES.

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There are two references in the literature to compounds of zirconium and chromic acid. The first is by Weibull,<sup>1</sup> 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,<sup>2</sup> who reports that zirconium is easily precipitated by free chromic acid as a flocculent, orange-yellow precipitate, difficultly 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

<sup>1</sup> *Acta Univ. Lund.*, [II] 18, V 57 (1881-1882).

<sup>2</sup> *Monatsh. d. Chem.*, 18, 667 (1897).

of 3 preparations in which the sum of the zirconia and chromic oxide was practically constant while the ratio varied. His preparations gave the following results:

	I.	II.	III.
ZrO <sub>2</sub> .....	65.94	65.76	61.29
Cr <sub>2</sub> O <sub>3</sub> .....	15.11	15.45	19.39
Sum.....	81.05	81.21	80.68

A glance at the analyses would seem to lead rather to the conclusion that the water removed the zirconia if it had any effect at all, since in the order given it is the zirconia which decreases. This is not of material importance, however, as his conclusions are not justified by our experiments. His final conclusion was that salts of different preparation gave different results, which would mean that a definite compound or compounds were not obtainable by his methods.

#### Preparation of the Basic Chromate.

The first method tried for the preparation of the basic chromate by precipitation from solutions of the oxychloride proved unsatisfactory because of the persistent retention of chlorine, due doubtless to the absorptive properties of the basic compound formed.

Pure zirconium hydroxide, Zr(OH)<sub>4</sub>, was then prepared, avoiding the use of hot water, as that renders it much less soluble. This was used in the form of a watery paste. It dissolved slowly in a concentrated solution of chromium trioxide. A portion of this placed in partial vacuum over a dehydrating agent yielded on prolonged standing a small amount of a reddish yellow precipitate. On diluting and boiling the nearly saturated chromic acid solution a precipitate was formed which was tinged with red, and further precipitation occurred on repeated dilution, the yellow becoming more pronounced. The precipitate was only slightly soluble and thorough washing left it a light yellow color without further change. The precipitate was not flocculent but granular, or possibly crystalline. The precipitation was carried out by filtering off the first precipitate, doubling the volume of water, and boiling. After the third addition practically no precipitate formed and the water was nearly colorless. Later, the method was changed and zirconium hydroxide was dissolved in a hot dilute solution of chromium trioxide. Further dilution and boiling brought down a yellow precipitate.

On heating these precipitates at 100-110° there was at first a rapid, then a continuous slow loss of water, the color changing from yellow to brownish yellow. It was evident that all the water was not driven off at 110° and that other changes were taking place. Furthermore, the samples heated to 110° were so difficultly soluble in hydrochloric acid that the accuracy of the chromium determinations was impaired. For

purposes of analysis, therefore, the preparations were placed on porous plates and air-dried to fairly constant weight. All of the water was not lost at  $100^{\circ}$ , but the remainder was lost at  $200^{\circ}$ . During the heating the color changed to a yellow-brown.

#### Analysis.

For the determination of the chromium the modified Bunsen method was used. The sample was introduced into a 60 cc. flask joined up with two U-tubes. A few pieces of large-grained magnesium carbonate were added and about 30 cc. of concd. hydrochloric acid. The U-tubes contained about 20 cc. of a 5% potassium iodide solution. The rubber used in the connections was boiled beforehand with potassium hydroxide solution to remove sulfur. After adding the hydrochloric acid to the sample the flask was slowly heated and in a few minutes the liberation of chlorine was complete. The liberated iodine was titrated with 0.1 *N* thiosulfate solution. The thiosulfate was standardized with pure potassium chromate and dichromate.

For the determination of the zirconia a sample was dissolved in concd. hydrochloric acid and boiled, then diluted, precipitated with ammonium hydroxide, filtered, dried, ignited, and weighed. This gave the total weight of zirconia and chromic oxide. The weight of zirconia was obtained by subtracting the chromic oxide determined in a similar sample.

Preparation A was washed with 4 l. of water, put on a porous plate and air-dried. The color was not clear yellow but slightly tinged with red. Portions were weighed out at the same time for determining water, chromium trioxide and zirconia plus chromic oxide. The water was determined by loss at  $200^{\circ}$ .

Preparation B was washed 8 times with about one l. of water each time. Preparation C was similarly treated. The analyses were made in duplicate.

		I.	Water-free.	II.	Water-free.
A	% CrO <sub>3</sub> .....	15.87	21.87	15.58	21.48
	ZrO <sub>2</sub> .....	56.40	77.75	56.64	78.09
	H <sub>2</sub> O.....	27.52	...	27.40	...
B	% CrO <sub>3</sub> .....	14.91	20.79	14.86	20.55
	ZrO <sub>2</sub> .....	56.82	79.21	57.44	79.45
	H <sub>2</sub> O.....	28.00	...	28.40	...
C	% CrO <sub>3</sub> .....	15.09	20.84	15.11	20.91
	ZrO <sub>2</sub> .....	57.34	79.15	57.15	79.09
	H <sub>2</sub> O.....	27.09	...	27.35	...

The differences in the results obtained for Preparation A are doubtless due to imperfect washing. Each preparation was distinct from the dissolving of zirconium hydroxide in a solution of chromium trioxide on through the precipitation and the washings, and the concentration of the solution of chromium trioxide also varied.

It is evident that a definite compound is secured by this method even though not absolutely pure. Making the comparison first on the water-free basis we have:

	A.		B.		C.		Average.	Zr <sub>2</sub> O <sub>3</sub> .CrO <sub>4</sub> .
% CrO <sub>3</sub> ....	21.87	21.48	20.79	20.55	20.84	20.91	21.08	21.16
% ZrO <sub>2</sub> ....	77.75	78.09	79.21	79.45	79.15	79.09	78.79	78.84

A comparison on the analysis direct would be:

	A.		B.		C.		Average.	$\frac{2ZrO(OH)_2}{ZrO.CrO_4.8H_2O}$ .
CrO <sub>3</sub> ....	15.87	15.58	14.91	14.86	15.09	15.11	15.40	15.35
ZrO <sub>2</sub> ....	56.40	56.64	56.82	57.44	57.34	57.15	56.97	58.54
H <sub>2</sub> O....	27.52	27.40	28.00	28.40	27.09	27.35	27.63	27.64

Close accord in results was not to be expected when air-dried samples were used for analysis. The deduction seems justified, however, that when chromium trioxide and zirconium hydroxide are mixed in varying proportions in the presence of an abundance of water there is a tendency to form the insoluble basic chromate  $2ZrO(OH)_2.ZrO.CrO_4.8H_2O$ , and that the favoring conditions are increase of temperature and excess of water. This precipitation of basic compounds of zirconium under these conditions, especially by boiling, is well known in cases of other acid radicals especially organic.

Perhaps for the basic chromate the following steps in the reaction may be indicated: First, the formation of the normal chromate  $Zr(CrO_4)_2$ , which is immediately hydrolyzed to  $ZrOCrO_4$ . Some of the  $Zr(OH)_4$  is also partially dehydrated to  $ZrO(OH)_2$  and the insoluble combination of these two substances is precipitated as  $2ZrO(OH)_2.ZrO.CrO_4.8H_2O$ .

#### Summary.

1. The results obtained would seem to controvert those of Haber.
2. A definite basic zirconium chromate is obtained on diluting and boiling solutions of zirconium hydroxide in chromic acid, to which the formula  $2ZrO(OH)_2.ZrO.CrO_4.8H_2O$  may be assigned.

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## THE QUANTITATIVE ANALYSIS OF SMALL QUANTITIES OF GASES.

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In some work on the study of gases in metals it was considered desirable to heat the metal in a cold envelope in order to eliminate as far as possible all sources of error. The most convenient method of doing this was by the passage of an electric current through the metal specimen itself. This and other conditions made necessary the use of small quan-