hydrogen with sulfur, and the tendency of the latter to polymerize, these oxidizing agents might abstract hydrogen from two of the ions HSO_3^{--}, and the two residues might then unite to form the ion of dithionic acid, $S_2O_6^{--}$.

In conclusion it may be stated that the differences in the oxidation of sulfite by iodine and iodate on the one hand and by permanganate, chromate and bromate on the other are due to fundamental differences in the characters of the two classes of oxidants, and these, are not to be altered by varying such secondary conditions as concentrations, temperatures, acidity or excess of the oxidizing agents. It therefore seems that attempts to work out accurate volumetric methods of determining sulfite with permanganate, bromate and dichromate along ordinary lines will probably prove futile.

The writer has received in this work the efficient aid of Mr. Neil L. Crone, a senior in Grinnell College.

Summary

This paper describes the continued work of the author on the oxidation of sulfurous acid, and gives the results obtained with bromate, dichromate and iodate in acid solution. The amounts of bromate and dichromate are less than those required by theory for the complete oxidation to sulfate—to about the same degree as that found for permanganate. The discrepancy is regarded as probably due to the same cause, the formation of some dithionic acid which resists further oxidation. On the other hand, iodate oxidizes completely the sulfite to the sulfate ion; this fact permits the very simple and accurate determination of sulfite by use of this oxidant.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

THE CAPILLARY RISE OF WATER IN TUBES OF VARIOUS METALS

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In a paper published some years ago, Bigelow and Hunter[1] presented results which tended to show that water and benzene rose to greater heights in capillary tubes of various metals than in tubes of glass. Unless metals are able to affect the surface tension of these liquids it is difficult to see how their results can be correct, unless all previous measurements with glass tubes are found to be in error. The most likely source of such an error would be a contact angle between the liquid and the glass, if it were not that it has been fairly well established that this angle of contact is zero. The fact that the magnitude of the effect obtained by Bigelow and Hunter

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[1] Bigelow and Hunter, *J. Phys. Chem.*, **15**, 367 (1911).

follows the electromotive series of metals made it appear possible that this effect might be due to some actual change in the surface tension caused by the metals. It was therefore thought worth while to repeat the measurements of Bigelow and Hunter.

Their apparatus is shown in Fig. 1.

The tube B was lowered by means of the clamp C into a beaker of the liquid until the top of the tube was exactly level with the liquid surface. A metal or glass plate A containing an accurately measured hole was placed on the top of the tube. The tube B was then slowly raised. The liquid rose in the tube until it just reached the height to which it would rise in a capillary tube of the same bore as the hole in the plate, when it broke loose. By means of the ratchet micrometer, D and E, this height could be accurately determined.

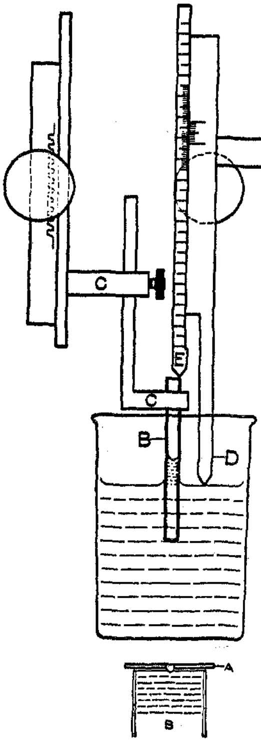

Fig. 1.

In order to avoid the construction of the measuring device used by Bigelow and Hunter and with the hope of increasing the accuracy of our measurements we decided that instead of raising the tube we might lower the level of the liquid in the containing vessel. By weighing the amount of liquid withdrawn, the distance through which the liquid surface was lowered could be determined if the vessel were properly calibrated.

Our apparatus is shown in Fig. 2.

The apparatus was carefully leveled till the tube was vertical. The liquid was withdrawn through the siphon until the top of the tube B came into contact with the liquid surface. The plate A containing the capillary hole was placed on the tube B and the liquid siphoned into a weighing flask until the meniscus broke loose from the capillary hole.

The ratio between the amount of liquid withdrawn and the lowering of the liquid surface was determined as follows. A depth micrometer accurate to 0.01 mm. was clamped above the liquid with the plunger just touching the surface. A portion of the liquid was withdrawn and weighed. The plunger was screwed down until it again touched the sur-

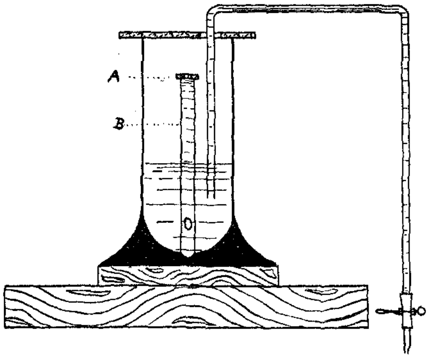

Fig. 2.

face. This was repeated over the vessel as far as it could be used. Our tube was uniform to within the error of our readings. While the calibration was being carried out, the siphon tube was kept in the vessel and a plate which contained no hole was placed over the tube B.

Plates of zinc, copper, silver and glass were used. The metal plates were ground flat on the lower side with carborundum flour on a glass plate. A hole about 2 mm. in diameter was drilled almost through each plate from the top and then a small hole was drilled through the remaining portion with a jeweller's pivot drill. The holes were reamed out with a needle and the rough edges removed with a carborundum razor hone. The holes were measured in 12 different diameters using a filar micrometer microscope, and the arithmetical mean of the 12 diameters was used. A stage micrometer served to standardize our filar micrometer. The holes we obtained were slightly elliptical, with a major axis from 1.2 to 2% greater than the minor axis. It has been shown by Richards and Carver[2] that this would give no greater error than 0.001%. The glass plates were made by melting down a very thick capillary until the hole was closed. The disk was cut out of the tube where it was almost closed and then ground down until the hole was of the desired size. By this procedure a conical hole was obtained so that the smaller diameter, that is, the one which really determined the capillary height, would be at the lower side of the disk. As our object was merely to test the effect of the various metals on the capillary rise, the apparatus was not thermostated for most of the results, but the temperature of the water was taken before and after each reading and the results were corrected[3] to 20°.

All glass parts were cleaned with chromic acid cleaning solution and

TABLE I

GLASS PLATE

r	H_2O G.	H	Temp. °C.	rh (corr. to 20°)
0.2998	135.79	49.36	22.8	14.87
..	135.85	49.38	23.1	14.89
..	135.84	49.38	23	14.88
..	135.76	49.35	23.2	14.85
..	135.79	49.36	23.1	14.86
..	135.81	49.36	23	14.86
..	135.80	49.36	23.2	14.87
			Av.	14.87
		Best value of other investigators[a]		14.88

[a] Richards and Coombs, THIS JOURNAL, **37,** 1668 (1915). Ref. 2. Harkins and Brown, *ibid.*, **41,** 499 (1919).

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[2] Richards and Carver, THIS JOURNAL, **43,** 827 (1921).

[3] The temperature coefficient used was that observed by Richards, Speyers and Carver, *ibid.*, **46,** 1196 (1924).

thoroughly rinsed with conductivity water. The metal plates were washed with distilled water, alcohol and ether and dried over a Bunsen flame. Carefully cleaned platinum forceps were used in handling the plates. Table I shows the results for a series of measurements with a glass plate, indicating the agreement between determinations. Table II shows the average results for the various metals together with the results of Bigelow and Hunter for these metals.

As will be seen from Table II, we were unable to verify the effect observed by Bigelow and Hunter. Thinking that possibly some galvanic effect might have occurred in their apparatus which was absent in ours we tried applying a potential from a platinum electrode in the liquid to the metal plate, but until bubbles were actually formed no effect was observed on the capillary rise.

TABLE II

AVERAGE OF RESULTS

Substance	rh (20°)	rh (Bigelow and Hunter)
Zinc	14.85	15.15
Copper	14.85	15.11
Silver	14.84	14.75
Glass	14.86	14.09

The most surprising result of this work was the accuracy and speed of the method. Measurements of surface tension accurate to within 0.2% could be obtained in two or three minutes. The capillary plates could be made and measured in a day. The standard of reference for the capillary height was a cheap, commercial micrometer instead of the expensive cathetometer, while the actual measurements are made by weight rather than height. The obvious disadvantage is that about 200 cc. of liquid is necessary. Where this is not objectionable the method is probably the quickest and easiest of the accurate methods for the measurement of surface tension.

Summary

1. It has been shown that water and benzene rise to the same height in tubes of glass and various metals.
2. An accurate and easy method of measuring surface tension has been described.

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