

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]
**A SUSPOSED EFFECT OF THE FORM OF CONTAINER UPON
THE DENSITY OF A GAS.**

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From his first series of determinations of the volumetric ratio in which oxygen and hydrogen combine to form water, Morley¹ found a mean value of 1 : 2.00023, the volumes being calculated to standard conditions of temperature and pressure. In his experiments the gases were measured, saturated with water vapor, in a eudiometer tube which was enclosed in a water jacket. Scott,² a few years later, reported the value 1 : 2.00285 for this ratio, the gases being measured moist but in a spherical vessel. In neither of these cases does the "probable error" of the mean exceed one part in twenty-five thousand. The value found by Scott agrees with the value which may be calculated from Morley's later results on the atomic ratio of oxygen and hydrogen, taken together with his value for the ratio of the densities of the two gases. In Morley's determination of the densities the gases were dried and measured in globes. The difference between the values obtained by Scott and by Morley is equal to one part in one thousand, or twenty-five times the value of the "probable error" in either determination.

In attempting to account for the discrepancy in these values, Morley³ suggests that the shape of the vessel may, in some way, be responsible, the effect being due to the attraction upon the gas, either of the walls of the container or of the water surrounding the vessel. Assuming this explanation to be correct, the effect of the shape of the containing vessel as measured in the ratio of the combining volumes is a differential one, and the effect should manifest itself in the case of at least one of the gases. In other words, if the gas is measured in a tube, then transferred to a bulb, and placed under the same temperature and pressure, the volume occupied by the gas in the bulb would differ from that which it occupied in a tube, and this difference would amount, in the case of one of the gases, to at least one part in a thousand.

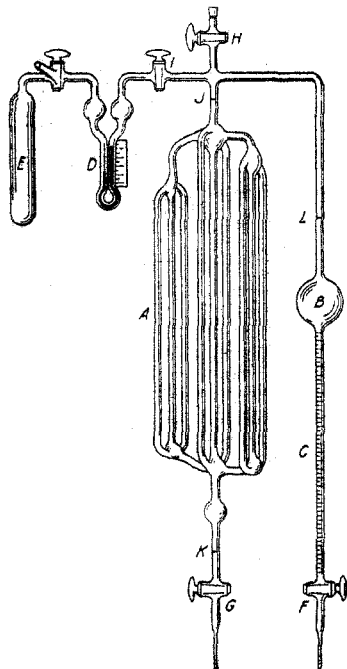
We have devised an apparatus to measure the volume of a certain quantity of gas contained in a system of tubes as compared with the volume occupied by the same quantity of gas when contained in a bulb. The tube system A (see figure) consists of nine tubes having a total length of about 470 cm. and an average internal diameter of 6.6 mm. To the lower side of the bulb B, which has about the same capacity as the system

¹ *Am. J. Sci.*, 41, 220 (1891).

² *Phil. Trans.*, (A) 184, 543 (1893).

³ "On the Densities of Oxygen and Hydrogen, etc.," *Smithsonian Institution*, 1895, p. 82.

of tubes, is fused a graduated tube of small internal diameter, C. The two systems are connected by capillary tubing, which also connects a sulfuric acid manometer, D, on the other side of which is an elongated bulb, E, made from large-sized tubing. The volume of this bulb is ap-



proximately the same as either the tube system A or the bulb B. The volume of the tube was defined by two scratches in the capillary tubing J and K, one above and one below the enlarged portion. The volume of the bulb system was defined at the top by a scratch on the capillary L, the lower limit being variable through the length of the graduated tube. Thus, after careful calibration it was possible to determine the point on the graduated tube which should limit the volume of the bulb system to make it just equal that of the tube system.

The volume of each of the two systems was determined by filling with mercury, then weighing the amount which had to be drawn off in order to lower the level to the lower mark. To make sure that there was no error in the determination of the volume due to a distortion of the glass by the weight of the mercury, the calibration was also made with water. To accomplish this the capillary leading to the manometer was cut so as to permit the apparatus being suspended from the beam of a large balance, from which the front and rear doors had been removed. The errors in the determination of the volume by this method were much larger than when mercury was used, but the results serve to show that there is very little, if any, distortion by the mercury.

The method of comparing the volume occupied by a gas in the two systems was as follows: After the entire apparatus had been filled with the gas to be measured, the mercury was admitted through F until the bulb system was filled, and through G until it reached the lower mark of the tube system. The stopcock H was then closed and the height of the sulfuric acid noted by means of a small scale attached to the manometer which was read by means of a cathetometer. The mercury was then allowed to rise in the tube system until it reached the upper mark and the mercury in the bulb system was allowed to fall until it reached a point in the calibrated tube nearly corresponding to the volume of the tube system. The manometer was then read and the mercury set at another

point in the graduated tube and the manometer again read. From these two readings a simple interpolation gave the point at which the mercury should have been set to give the pressure initially present in the tube system. The gas was immediately returned to the tube system and the manometer again read. In case this reading indicated a decided change in pressure the measurement was discarded, but if only a small change was noted the mean of the two readings was taken for the interpolation. A change in pressure between the first and second readings in the tube system indicated, of course, a relative change in temperature between the tube system and the bulb E which would vitiate the result.

For the first series of measurements the entire apparatus, with the exception of the leveling bulbs, was enclosed in a box with a glass door. The case also contained a motor-driven fan which provided a rapid circulation of air. Thus while it was not possible to maintain a constant temperature during the transfer of the gas, the results were not affected, since the temperature of E changed with that of the bulb and tube system. Four series were run, air and hydrogen both being used dry as well as saturated with water vapor. While slight differences in volume were noted in the two systems the largest mean is less than one part in ten thousand, which is the order of our experimental error and could not explain the disagreement referred to above.

Following a suggestion of Professor Morley¹ that the abnormality might be due to the attraction of the water which surrounded his eudiometer tube, we enclosed both our systems in a water jacket. This was made of wood, with glass front and back, the bottom being made in two parts to allow the setting in place of the glass apparatus. For setting the glass, as well as making the other joints water tight, we found a mixture of equal parts of rubber and rosin, melted together, very satisfactory. Where greater strength is required the amount of rubber is decreased. The box when finished had a capacity of about twenty liters, so that when filled with water it could be maintained at a very constant temperature. The bulb E was also surrounded with water contained in a two-liter Dewar flask. As would be expected, the individual determinations do not vary as far from the mean as in the first series. It may be seen from the results of this series that any difference in volume which may be indicated is not larger than one part in 20,000. The small differences in volume which are shown by the results may be due to small bubbles of air which remained between the mercury and the glass when the level of the former was raised, and which were so small or so placed as to escape detection. The gases used were not carefully purified as it was assumed that the small amounts of impurities which might be present would have no bearing on the effect which we were attempting to measure.

¹ Private communication.

Experimental.

CALIBRATION OF THE TWO SYSTEMS, VOLUMES CALCULATED TO 20°.

Tube system measured with water.		Tube system measured with mercury.	
178.498 cc.		178.509 cc.	
178.515		178.511	
178.507			
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Mean,	178.507 cc.	Mean,	178.510 cc.

Bulb system measured with water to calibration 0.400.		Bulb system measured with mercury to calibration 0.400.		Bulb system measured with mercury to calibration 1.658.	
178.115 cc.		178.119 cc.		179.378 cc.	
178.128	Volume to zero		Volume to zero		
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	on scale,	177.719 cc.	on scale,	177.720 cc.	
Mean,	178.121 cc.				

The tube system was accidentally broken before the last two sets of determinations had been made, which necessitated a new calibration of this part after the apparatus had been repaired. This was done with mercury and gave the value 178.586 cc.

COMPARISON OF VOLUMES, APPARATUS IN AIR.

Dry Air.			Dry Hydrogen.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.507 cc.	-0.003 cc.	178.510 cc.	178.492 cc.	-0.018 cc.
	178.503	-0.007		178.505	-0.005
	178.500	-0.010		178.500	-0.010
	178.501	-0.009		178.494	-0.016
	178.506	-0.004		178.490	-0.020
	178.501	-0.009		178.519	+0.009
	178.490	-0.020		178.513	+0.003
	178.515	+0.005		178.513	+0.003
	178.002	-0.008		178.505	-0.005
	178.515	+0.005		178.502	+0.008
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Mean,	178.504 cc.	-0.006 cc.	Mean,	178.503 cc.	-0.007 cc.

Air, Saturated with Water Vapor.			Hydrogen, Saturated with Water Vapor.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.508 cc.	-0.002 cc.	178.510 cc.	178.508 cc.	-0.002 cc.
	178.496	-0.014		178.498	-0.012
	178.488	-0.022		178.506	-0.004
	178.489	-0.021		178.492	-0.018
	178.506	-0.004		178.505	-0.005
	178.484	-0.026		178.498	-0.012
	178.494	-0.016		178.494	-0.016
	178.496	-0.014			
	178.512	+0.002			
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Mean,	178.497 cc.	-0.013 cc.	Mean,	178.500 cc.	-0.010 cc.

DETERMINATIONS WITH APPARATUS IN WATER BATH.

Gas, Dry Oxygen.			Dry Hydrogen.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.509 cc.	-0.001 cc.	178.510 cc.	178.509 cc.	-0.001 cc.
	178.507	-0.003		178.514	+0.004
	178.515	+0.005		178.523	+0.013
	178.511	+0.001		178.518	+0.008
	178.518	+0.008		178.520	+0.010
	178.512	+0.002		178.518	+0.008
Mean,	178.512 cc.	+0.002 cc.	Mean,	178.517 cc.	+0.007 cc.
Oxygen, Saturated with Water Vapor.			Hydrogen, Saturated with Water Vapor.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.586 cc.	178.599 cc.	+0.013 cc.	178.586 cc.	178.594 cc.	+0.008 cc.
	178.591	+0.005		178.595	+0.009
	178.586	+0.000		178.601	+0.015
	178.597	+0.011		178.585	-0.001
	178.590	+0.004		178.599	+0.013
Mean,	178.592 cc.	+0.006 cc.		178.576	-0.010
			Mean,	178.602	+0.016
			Mean,	178.593 cc.	+0.007 cc.

Summary.

We have compared the volume occupied by a gas in a system of tubes with that which it occupies in a bulb, in an effort to explain the difference in the volumetric ratio of hydrogen to oxygen in water as determined by Morley and by Scott. We have shown that there is no difference in volume larger than one part in ten thousand, whereas the two determinations referred to differ by one part in one thousand.

URBANA, ILL.

THE DENSITY OF AQUEOUS SOLUTIONS OF COPPER SULFATE AND SULFURIC ACID.

BY H. D. HOLLER AND E. L. PEFFER.¹

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I. INTRODUCTION.

In connection with an investigation on the regulation of solutions for electrodeposition, especially of acid copper sulfate solutions for electrotyping, it was found desirable to devise a simple method of determining and adjusting their composition. Since the solutions usually employed for the above purpose contain only copper sulfate and sulfuric acid, the composition of any given solution is fixed if the acid content and density at a given temperature are known. The density can be readily determined with a hydrometer, and the acidity can be ascertained with sufficient

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