of Mines method 3 electroscope chambers, each of which was measured with 2 interchangeable leaf chambers.

3. The same chambers and heads were standardized against U. S. Bureau of Mines standard pitchblende from Colorado.

4. The results give as final average of 18 determinations $3.40 \times 10^{-7} \pm 0.03$ for the ratio radium : uranium. The result agrees with the average of Becker and Jannasch, 3.399×10^{-7} obtained at the Radiological Institute at Heidelberg, using standard radium salt from the Institute of Radium Research in Vienna, and with the old uncorrected value 3.4×10^{-7} of Rutherford and Boltwood.

The writers express with pleasure their indebtedness to Messrs. J. P. Bonardi and J. E. Conley for their kindness in recrystallizing the 100% radium bromide from which the pure radium chloride was prepared, and also to Dr. N. E. Dorsey, of the U. S. Bureau of Standards, for making the γ-ray comparison with the International standard.

GOLDEN, COLORADO.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

A WEIGHT BURET FOR GAS ANALYSIS.[1]

BY E. R. WEAVER AND P. G. LEDIG.

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The use of a weighing method for making gas measurements was suggested by the great advantages of a weight buret for liquids over the older volumetric burets. The apparatus here described was designed primarily for use in a forthcoming study of gas-analysis methods; but it appears to have sufficient application, for any gas volumetric measurements requiring greater precision than is easily obtainable with an ordinary gas buret, to warrant publication at this time. A description of the apparatus and its method of use will first be given; then the reasons for various details of construction will be considered; the principal sources of error will be pointed out; and finally some typical experimental results which show the precision obtainable will be given.

Description and Method of Use.

For the sake of clearness, the apparatus is represented in Fig. 1, as though constructed in a single plane. Actually, the tubes and bulbs may be arranged in any convenient manner, if the relative levels of the different parts are kept approximately as shown. In the apparatus constructed all the parts which had to be water-jacketed, fitted neatly into a round battery jar of about twice the diameter of Bulb A.

By means of connections to vacuum and air pressure, which are sup-

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[1] Published by permission of the Director of the Bureau of Standards.

plied by a small motor-driven pump, mercury may be drawn into or forced out of Bulbs B or D through Stopcocks *c* and *e*. When the apparatus is ready for use, Bulb A and Tubes 1, 3, 4 and 5 are completely filled with mercury, which also fills Tube 6 nearly up to the contact point *p'*. When, as is usually the case, the gas is to be measured saturated with water vapor, a drop of water is included in the compensator C, and a little water is allowed to wet the walls of the buret.

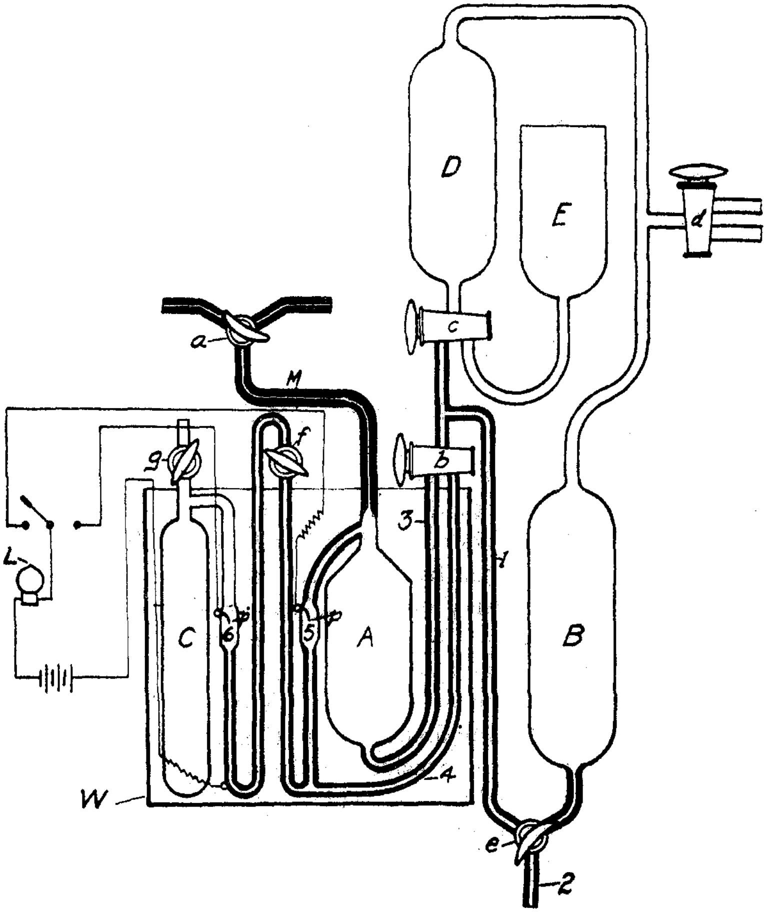

Fig. 1.

The method of making a gas measurement is as follows. With Stopcock *f* open, the level of the mercury in Tube 6 is carefully adjusted to exactly close the contact at *p'* by running in mercury from D. Stopcocks *f* and *g* are then closed, confining a fixed volume of gas in the compensator C. The measuring Bulb A is now connected through *a* with the vessel containing the gas to be measured and mercury is withdrawn into

D until the surface of separation of the gas and the confining liquid in the buret reaches the mark M. Stopcock *c* is now closed; Stopcock *e* is turned to connect A and B and the gas is drawn into A, the mercury displaced flowing into B. The surface of separation between the gas and the confining liquid following the gas is stopped just at mark M by closing Stopcock *a*. The volume of mercury in B is now exactly equal to the volume of gas in A; it remains to run mercury from B to A until the pressure of the gas in A is adjusted to equal that in the compensator C. Mercury is first drawn into B through Tube 4 until the contact point in 5 is uncovered; then it is forced back until the contact is just closed as shown by the electric light L. The amount of mercury in the compensator between points 5 and 6 is thus accurately adjusted. Stopcock *b* is closed to Tube 4 and opened to Tube 3; Stopcock *f* is also opened; and by running mercury between A and B through Tubes 1 and 3 the pressure in A is carefully adjusted, until the contact in 5 is again just closed, final adjustment always being made with a rising meniscus. Assuming that contact-points p and p' are on the same level, the pressure of the gas in A is now exactly equal to that in compensator C, and its volume is exactly equal to the volume of the mercury in B. Stopcock *e* is turned to connect B to Tube 2 and the mercury run into a small flask in which it is weighed. From the weight found, the volume of the mercury, equal to the volume of the gas in A, is easily determined.

The process of adjustment appears very tedious on paper, but really does not require much more time of an observer familiar with the apparatus than does the adjustment and reading of an ordinary buret using a Peterson compensator. Bulb D is merely a mercury reservoir into which mercury can be introduced at will through Funnel E. When the gas is to be transferred from A to an absorbing pipet or other container, Stopcock *f* is closed, Tube 5 is filled with mercury run from D through Tube 4 and finally the entire volume of gas in A is displaced with mercury introduced from D through Tube 3.

Merits of the Apparatus.

The apparatus has the following advantages.

1. The measurement of the actual volume of gas is very accurate, the probable error being ordinarily much less than the probable error in making the pressure adjustment. This measurement is independent of the condition of the meniscus, of whether water or other liquid is present on top of the mercury, of drainage, and of drops of liquid sticking to the walls of the measuring vessel.

2. Small volumes are measured directly and with great accuracy; a pressure correction is of course necessary when the volume is less than that of the tubes between Mark M and contact-point p.

3. The observer can form no idea what his results will be until he has

weighed the mercury. If a proper balance is used this final measurement is not subject to an appreciable observational error, consequently the observer is entirely unbiased by any notion of what the result should be.

4. The reading does not depend in any way upon the reading of a graduated scale and is, therefore, free from errors of calibration and errors due to parallax.

5. The apparatus is short and compact; the changes of mercury level, being small, are easily made by means of air-pressure adjustments; and the difficulty of reading a long vertical scale is eliminated.

6. The apparatus is easily jacketed in a jar of convenient size and shape. No connection goes through the jacket, which can be removed at once for cleaning or repairing the apparatus; this also eliminates any difficulty in making the jacket water-tight.

7. The apparatus, if properly constructed, can be completely drained of mercury and filled with a cleaning solution without disturbing any of the connections.

8. The gas to be measured is never in contact with a stopcock, rubber tube, or other possible source of leakage except while being transferred through Stopcock A, and it is easy to avoid excessive pressures either above or below atmospheric when making this transfer.

9. The gas is always completely expelled from the buret when it is transferred to a pipet or other container. This eliminates one of the principal disadvantages of the familiar Peterson compensator in which there is a considerable residual volume of gas which can be transferred only by tedious and careful manipulation, and at the risk of spoiling the compensation by running mercury from the compensator into the buret.

10. The surface of the mercury at p, can always be made fresh by forcing mercury into A through Tube 4, and that without transferring the gas sample or affecting the filling of the compensator. This is very important where an electrical contact is used in adjusting the compensator and would be of value even if the mercury in the compensator were adjusted to a line on the glass.

11. There are no rubber connections to foul the mercury or to give trouble in other ways.

12. The apparatus may be made of any desired capacity without loss of accuracy, and no facilities for graduating it are required as in the case of a special volumetric buret.

Details of Design.

In general, the dimensions and other details of construction of the apparatus are determined only by convenience and have little to do with the accuracy of the measurement. The platinum points p and p' must be on very nearly the same level, otherwise an error results in the compensation for changes of temperature, amounting to about one part in 20,000 of the volume measured per degree change in temperature per millimeter difference in levels. Obviously it is not difficult to so adjust the levels of these points that this correction will be negligible under ordinary conditions.

Experiments which need not be described here were made to determine the relative accuracy and convenience of adjusting the mercury surface in the compensator to a line, adjusting to make visible contact with a glass or metal point, and adjusting to make electrical contact as proposed by Gregg.[1] It was found that the last mentioned method generally gave the greatest accuracy and was by far the most convenient. This method was, therefore, adopted; practically the only objection to it is the possibility of a little dirt such as a particle of stopcock grease, adhering to the platinum point and changing the height at which the mercury meniscus makes contact.

The approximate diameter of the enlarged portions of Tubes 5 and 6 required to give minimum error was also determined experimentally; the point is hardly of sufficient importance to justify a description of the several methods employed. It is sufficient to state that it was found that the minimum average error occurred with tubes having diameters from 8.5 to 13 mm., there being little difference over this range. The average error was much greater with tubes of much smaller diameter because of the tendency of the mercury to stick to the walls; tubes larger than 13 mm. gave increasing errors because of the effect of any error in adjusting the levels, upon the relative volumes of compensator and buret. A diameter of one cm. was chosen for these tubes and appears to be about right for a measuring vessel of not over 150 cc. capacity.

A large compensator-volume is, of course, favorable to accurate results because any error in adjusting mercury levels makes less relative difference in the volume of gas confined; but the advantage of making it larger than 25 cc. is not great. In order to accommodate all necessary parts within the jar selected for a water jacket, the compensator actually constructed has a volume of about 35 cc.

The apparatus for supplying positive and negative pressure is shown diagrammatically in Fig. 2, which is practically self-explanatory.

Sources of Error.

It is not proposed to thermostat the apparatus because, with the changes of temperature occurring in the ordinary use of the instrument, the errors in compensation due to temperature change are less than the accidental errors of pressure adjustment. With the apparatus as now constructed the following remaining sources of error may be mentioned.

1. Errors in setting the meniscus to the mark M on the inlet capillary. This error enters twice into every measurement.

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[1] *J. Ind. Eng. Chem.*, **9**, 528 (1917).

2. Errors due to incorrect adjustment of the mercury levels. Since there are 3 adjustments, there are 3 chances of making this class of errors. These errors are due to (1) sticking of the mercury to the walls of the tubes,—probably the most important source of error involved in the whole method of measurement; (2) failure of the mercury to make instant contact with the platinum point because of a film of dirt on mercury or platinum; (3) the effect of impurities upon the surface tension of the mercury and the height of the meniscus; (4) running past the point of contact, the amount of the error depending upon the speed of flow of the mercury, the time required for the miniature lamp to come to incandescence, and the reaction time of the observer. Errors in adjusting the mercury levels affect the measurement in 3 ways, (*a*) by destroying the equality of pressure between the compensator and measuring bulb, (*b*) by changing the volume of the compensator, and (*c*) by including in the compensating tube mercury which should have been run into B and weighed, or *vice versa*. If exactly the same procedure is always employed, these errors of adjustment are likely to be very nearly the same in successive measurements and, therefore, tend to cancel out when the measurements are compared.

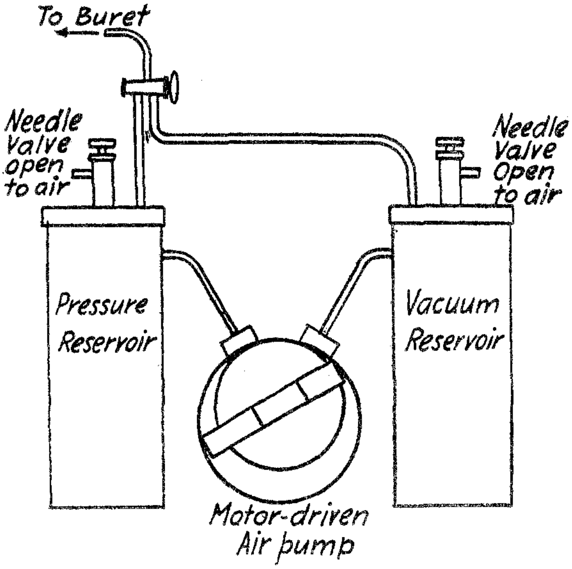

Fig. 2.—Pressure system for operating weight buret.

3. Errors in collecting the mercury because of small drops adhering to the glass, small gas bubbles trapped in Tubes 1 and 3 which vary in size with variations of static pressure; and errors of weighing.

4. Errors due to changes of temperature of the system as a whole. Since comparative measurements only are wanted in most work, no error of this class occurs if the temperature is the same when each of the measurements is made. These include (1) change in the density of the mercury because of thermal expansion; (2) change in the volume of the compensator because of the thermal expansion of the glass; (3) change in the relative pressures in measuring bulb and compensator due to differences in the levels of p and p'; (4) errors due to differences in the coefficients of ex-

pansion of the gas in compensator and measuring bulb when the composition of the two is not the same. The first 2 sources of error in this group are easily corrected for if the temperature change is known. The following equation applies:

$$V_0 - V_1 = \frac{W\ (t_1 - t_0)(C_m - C_g)}{d}$$

where V_1 and V_0 are, respectively, the volume of the gas determined at t_1 and the volume which would have been determined had the measurement been made at t_0; W is the weight of mercury observed, d is the density of mercury at the temperature of measurement, and C_m and C_g are the coefficients of expansion of mercury and glass, respectively.

5. Errors due to differences of temperature in different parts of the system. These may be (1) local temperature differences in the water bath; (2) a difference in temperature between the mercury in A and the water bath which will disappear if enough time elapses after the introduction of the mercury, and (3) a difference in temperature between the bath and the outside air which principally affects the portion of the compensating tube leading to Stopcock *g*.

6. Errors due to the fact that the liquid unavoidably present on the surface of the mercury in the buret does not have the same vapor pressure as the water in the compensator.

Experiments to Determine Accuracy of Measurement.

For the purpose of determining directly the aggregate effect which may be expected from the many possible sources of slight error encountered, 2 series of experiments were made. In the first series the same mass of gas, confined over mercury, was repeatedly measured, being entirely transferred to a mercury-sealed receiver between each consecutive pair of measurements. In the second series, a mass of gas was measured as a whole and was then subdivided, each portion measured being discarded after measurement. In both cases a little pure water was used to saturate the gas in both buret and compensator.

A typical series of measurements of the first class is shown in Table I, in which the first column gives the temperature of the water jacket, the second gives the weight of mercury actually observed, the third gives the weight of mercury corrected only for thermal expansion as described above, the fourth gives the volume of gas computed from the corrected weight of mercury, and the fifth gives the difference between each measurement and the average of all the measurements.

Table II gives a summary of all the results obtained in the last 14 comparisons by the method illustrated in Table I. A large number of other comparisons were made with results nearly but not quite so concordant. Just previous to making the first comparison given in the table a minor

TABLE I.

Typical Set of Measurements of a Single Volume of Gas.

Temperature. °C.	Weight of mercury. Observed. G.	Weight of mercury. Corrected. G.	Volume. Cc.	Deviation from average. Cc.
18.7	1130.10	1130.10	83.405	−0.006
18.8	1130.16	1130.17	83.411	0.000
18.9	1130.10	1130.14	83.408	−0.003
19.1	1130.09	1130.16	83.410	−0.001
19.1	1130.26	1130.33	83.423	+0.012
19.2	1130.06	1130.15	83.409	−0.002
19.5	1129.96	1130.10	83.405	−0.006
19.6	1130.05	1130.21	83.414	+0.003
19.6	1130.10	1130.17	83.411	−0.000

Average volume 83.411.

Average deviation from average........ ±0.0037 cc.
0.0044%.

Greatest deviation from average........ 0.012 cc.
0.014%

alteration in the construction of the apparatus was made which is believed to have slightly improved its accuracy, hence the results here given represent all the comparisons of this kind made with the apparatus as described.

TABLE II.

Volume measured. Cc.	Number of measurements.	Average deviation from average. %	Average deviation from average. Cc.	Greatest deviation from average. %	Greatest deviation from average. Cc.	No. of measurements deviating as much as 0.01 cc.
98.910	7	0.006	0.006	0.014	0.014	2
88.349	4	0.005	0.004	0.008	0.007	0
87.329	10	0.005	0.004	0.014	0.012	1
85.539	4	0.001	0.001	0.002	0.002	0
83.411	9	0.004	0.004	0.014	0.012	1
83.306	9	0.006	0.005	0.014	0.012	1
81.388	7	0.004	0.004	0.009	0.008	0
77.261	4	0.007	0.005	0.009	0.007	0
75.498	4	0.002	0.002	0.002	0.002	0
28.453	3	0.009	0.003	0.014	0.004	0
8.474	7	0.033	0.003	0.070	0.006	0
3.129	3	0.019	0.006	0.028	0.0009	0
1.413	2	0.026	0.0004	...	..	0
0.220	3	1.1	0.0024	1.8	0.0041	0
Total......	76	...	...	...	..	5

General average deviation of individual readings from average determination of same volume, 0.0034 cc.

In Table III are given the results obtained by measuring a volume of gas, then subdividing it into a number of portions each of which is measured. If there were any considerable systematic error it would be indicated by a difference between the measurement of the volume as a whole and the sum of the measurements of the partial volumes.

Table III.

Partial volumes measured	23.852	8.468	10.800	1.201
	24.942	11.379	5.268	0.219
	28.443	8.589	20.791	
			29.671	
			7.647	
			24.690	
Sum	77.237	28.436	98.867	1.420
Direct determination of total volume	77.244	28.443	98.881	1.413

The data presented in the above tables indicate a percentage accuracy on a sample of 100 cc. which is comparable with the accuracy of good titrimetric determinations.

Since the size and shape of the container in which the gas is measured are determined only by convenience, the method is obviously suited to the measurement of much larger volumes of gas than were here determined. Water can, of course, be used as the confining liquid with the usual limitations on account of solubility.

The apparatus can also be easily adapted as an accurate and convenient gas volumeter for determining the amount of gas evolved from a solid or liquid by any chemical reaction. For this purpose the weight of sample taken and the amount of gas confined in the compensator may be so related that the weight of confining liquid will be a simple multiple of the percentage of the constituent to be determined.

Summary.

An apparatus for conveniently determining small quantities of gas by weighing the confining liquid displaced is described and its percentage accuracy is shown to be comparable with the general accuracy of good titrimetric measurements.

Washington, D. C.

[Contribution from the Fixed Nitrogen Research Laboratory, Ordnance Department.]

THE ENTROPY OF GASES.

By Richard C. Tolman.

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From a thermodynamic point of view, the problem of chemical affinity may be considered as completely solved, as soon as we have determined the heat content and the entropy content of all the reacting substances in which we are interested. The solution of this important task has been greatly simplified by the work of Nernst and Planck in introducing the so-called third law of thermodynamics, which states that the entropy content of solids and liquids becomes zero at the absolute zero of temperature. This has made possible a determination of the entropy content of *solids* and *liquids* at any temperature merely from a knowledge of specific