

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS.]

A UNIVERSAL GAS-VOLUMETER.

BY HORACE G. DEMING.

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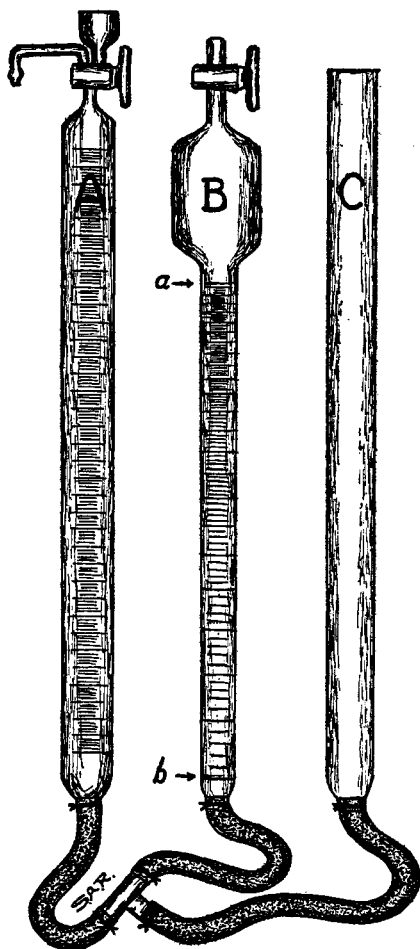
Historical.

One of the circumstances tending to prevent the more general use of gas-volumetric methods has doubtless been the fact that the calculations called for involve considerable labor or make necessary the use of extended reduction tables. The purpose of this paper is to show how a gas-volumeter may be made direct reading, the volume of the gas collected being not only reduced mechanically to standard conditions but converted automatically into the percentage of any desired constituent, no matter what the nature of the substance analyzed, for any weight of sample. The

instrument is thus one of quite universal applicability.

Before describing the construction of the new form of gas-volumeter, reference should be made to the similar instrument of Lunge.¹ This consists of three tubes, *A*, *B* and *C*, connection to a T-tube by means of rubber tubing. The tube *A* is graduated in cc. and serves to measure the gas, which is generally evolved in a separate piece of apparatus not shown in the sketch. The tube *B* is shaped like an inverted pipet, and consists of a bulb, continued below by a cylindrical tube graduated in cc. The tube *C* is simply a levelling-tube, for adjusting the pressure on the gas in *A*.

As commonly used, a quantity of air equivalent to 100 cc. at *standard conditions* is drawn into the tube *B* at the beginning of a series of experiments, the stopcock of the tube being then closed and sealed with mercury or wax. The gas (nitrogen, nitric oxide, carbon dioxide, oxygen, etc.), is drawn from the reaction vessel or from a gas-pipet into the measuring tube *A*. The stopcock at the top of



¹ *Z. angew. Chem.*, 3, 139-144 (1890).

A is then turned, and the levelling-tube *C* is raised until the mercury in *B* stands at the 100 cc. mark, at the bottom of the bulb. The air in *B* has thus been compressed to the volume it would occupy at standard conditions.

The measuring tube *A* is next adjusted until the mercury within it stands at the same level as the mercury in *B*. The gas in *A* is then under the same pressure as the air in *B*, and is therefore also compressed to the volume it would occupy at standard conditions, since all gases are equally compressible, within the limits of accuracy of this method. A part of the calculation otherwise necessary and the need for observing the temperature and pressure have thus been obviated, the reduction of the gas to standard conditions being accomplished mechanically.

A further saving of time in the use of this instrument has sometimes been effected by graduating the tube *A* in such a way that its subdivisions represent directly the number of mg. of the constituent to be determined. Such an instrument is, of course, restricted to a single kind of analysis. Or a weight of sample may be taken such that each cc. of gas, measured under standard conditions, will represent 0.2% or 0.5% of the constituent to be determined. However, the accurate adjustment to definite weight of such small samples as are needed for this kind of work will almost always require more time than would be needed for the extra calculation.

A proposed improvement in the instrument just described is the gravivolumeter of Japp.¹ In this the correction tube *B* contains the equivalent of 25 cc. of air under standard conditions, regardless of the substance to be determined. The mercury in this tube is however not brought to the 25 cc. mark, but to a point depending on the constituent to be determined. The pressure in the measuring-tube is therefore different from standard pressure, and the density of the contained gas is so altered that each cc. becomes equivalent to 1 mg. of the constituent to be determined. This instrument has the disadvantage that the gas in the measuring tube must be measured under a considerably reduced pressure, and there is therefore always danger of air leaking into the apparatus. The saving in time is moreover of slight advantage, since there still remains the labor of a division by the weight of the sample before the result of the analysis can be expressed as a percentage.

An obvious improvement would be to compensate for a varying weight of sample by compressing the air in *B*, and therefore the gas in the measuring tube *A*, to a volume depending on that weight. In this case the volume of air sealed off in *B*, at the beginning of a series of experiments, would depend on the constituent to be determined. The instrument here proposed is therefore merely a Lunge gas-volumeter, in which a scale of mg. has been substituted for the scale of cc. usually inscribed on *B*.

¹ *J. Chem. Soc.*, 59, 894 (1891).

The volume of gas collected in *A*, expressed in cubic centimeters, gives the percentage of any desired constituent directly, when the mercury in the correction tube has been adjusted to a mark corresponding to the weight of sample taken. This is moreover accomplished while measuring the gas under a pressure very nearly equal to that of the atmosphere. We shall next indicate how the tube *B* needs to be graduated in order to fulfill these conditions.

Graduation of the Correction Tube.

In the most general case, let the volume of air, reduced to standard conditions, drawn into the correction tube *B* at the beginning of a series of experiments, be V_s , and let the volume to which this air is compressed at the end of any given experiment, when the final reading is to be made, be V . Let the volume of the gas contained in the measuring tube *A*, at the same instant be N . Let the weight of the constituent to be determined, corresponding to 1 millimol of the gas collected, be M ; and let the weight of sample taken for analysis be W . The percentage of the constituent to be determined is then

$$\frac{V_s}{V} \cdot \frac{N}{22.38} \cdot \frac{100M}{W}.$$

Let us now so choose conditions that the volume of the gas collected may be simply related to the percentage of the constituent to be determined. We have then

$$N = k \cdot \frac{100 M V_s N}{22.38 V W},$$

$$\text{or } V_s = \frac{0.2238 V W}{k M}, \quad (1)$$

in which k is an arbitrary constant. Now, since this equation shows V to vary inversely with W , for constant V_s , the scale of weights to be inscribed in the tube *B* must be a reciprocal scale, *i. e.*, one defined by the equation

$$V = K/W, \quad (2)$$

in which K may be given any constant value that we please.

The tube itself may be of any convenient capacity, but the cylindrical portion must make up at least 60% of its entire volume. Let two marks, a and b , be made on the tube, near the upper and lower limits of the cylindrical portion. Let the capacity of the tube above these marks, determined by calibration with mercury, be respectively, V_a and V_b , the distance between the marks being d mm.

The point a is now given some value W_a , well above the maximum weight of sample likely to be met in any analysis to be carried out with the instrument. The value 500 mg. will probably serve in all cases. The constant K in Equation 2 must therefore evidently have the value

$V_a W_a$. If the tube below the point a be now assumed to be of uniform bore, it may be graduated with a dividing engine. The distance, in mm. from an origin $V_a d / (V_b - V_a)$ mm. above a to a mark representing any value W_x on the scale of weights to be constructed will then be

$$x = \left(\frac{V_a W_a d}{V_b - V_a} \right) \cdot 1/W_x. \quad (3)$$

If there is any doubt about the uniformity of the cylinder, the total volume above each of several marks may be determined, and the successive sections of the tube then graduated separately as here described for the entire interval ab .

When the quantity in the parenthesis above has been determined from the results of the calibration with mercury, the values for x will need to be worked out for each value of W_x from $W_x = W_a$ backward to 40% of W_a , for example, for each mg. from 500 mg. to 200 mg. This calculation may be completed in a little over an hour, using a table of reciprocals and a multiplying machine, or a nomon. Any apparatus manufacturer should be able to supply tubes graduated according to the preceding specifications at a slight advance over the price of the older form of instrument. Almost the only extra labor is in the calculation of the values of x in Equation 3, the calibration with mercury and the actual laying off of the calculated distances with a dividing engine being but little more troublesome than when a uniform scale is to be constructed.

Another method for graduating the scale B eliminates most of the calculation, and may be employed when a dividing engine is not available. Determine by calibration with mercury the volume of the tube above each of three points, a , b and c . Transfer these points with a pair of dividers to a straight line ruled on paper, and label them there with the corresponding values of W , calculated from Equation 2 above, assigning to K the value $V_a W_a$. Intermediate points may then be located mechanically, since Equation 2 is merely a special case of the general equation for a projective scale.¹ The scale thus constructed may then be transferred to the wax coating of the tube B , and afterward etched with hydrofluoric acid.² The practical value of this method will not depend altogether on whether the time required to graduate the tube in this way, amounting to three or four hours in all, is less than that likely to be saved in computation during the life of the tube; for a direct reading instrument will insure results free from errors in calculation, a result worth going to some trouble to obtain.

If the volume of air admitted to the correction tube at the beginning of a series of experiments be measured at other than standard conditions this volume will be

¹ Cf. preceding article, p. 2142.

² Ostwald-Luther, "Physiko-Chemische Messungen," 3rd Ed., p. 57.

$$V' = 760/P.T/273.V_s. \quad (4)$$

This volume will correspond to a point W' on the mg. scale whose construction has just been described, in which

$$W' = K/V'. \quad (2')$$

Combining Equations 1, 2, 2' and 4, we have

$$W' = 1.605 kMP/T. \quad (5)$$

This gives the point on the mg. scale to which the mercury in B must be brought when the tube is filled with air at the beginning of a series of experiments. In this equation M represents the weight of the constituent to be determined that is equivalent to one millimol of the gas to be collected; P is the atmospheric pressure, in millimeters of mercury, corrected for temperature and capillarity (and for aqueous tension when the gas to be collected is measured moist); T is the absolute temperature; and k is a constant (1, 2 or 5) so selected that the calculated value of W' falls within the limits of the scale on B . (This will always happen with one of these three values of k provided the calibrated portion of the correction tube is at least 60% of its total volume, as recommended above.)

Details of Manipulation.

The details of manipulation of the gas-volumeter whose construction has just been described are as follows:

At the beginning of a series of experiments open the stopcocks of A and B and introduce into B a drop of water if the gas is to be measured moist, or a drop of sulfuric acid if it is to be measured dry. Raise or lower C until the mercury in B stands at a mark W' , calculated from Equation 5. Close the stopcock of B and seal it with wax. When B has once been filled in this way it need not be changed during a series of experiments in which the same constituent is to be determined; but it should be checked occasionally by bringing the mercury in C to the same level as that in B , and noting whether the level at which the mercury now stands in B corresponds with the value of W' calculated from the temperature and pressure then obtaining.

Take a sample whose weight in mg. is approximately equal to the value of W' used in filling the correction tube. If this is done there is less danger of leakage, since the gas is finally measured under a pressure very nearly equal to that of the atmosphere. Let the gas be evolved in a separate vessel, and transfer it to A with the usual precautions.¹ Close the stopcock of A when the gas within it has been brought to atmospheric pressure by raising or lowering C . Next raise or lower C until the mercury in B is brought to a mark corresponding to the weight of sample taken, moving A at the same time so as to bring the mercury in it to the same level as that in B at the moment the adjustment is finished.

¹ Sutton, "Volumetric Analysis," 10th Ed., pp. 585-589.

Wait a few minutes for the gas to come to room temperature, during which time the second sample may be weighed out and placed in the decomposition tube; then make a final adjustment of *A* and *C*, placing the eye in such a position that the mercury in *A* may be observed to occupy the same level as that in *B* at the moment the mercury in *B* is finally adjusted to a weight corresponding to the exact weight of the sample taken. The three tubes being clamped in this position, the reading of *A* in cc. will give the percentage of the constituent to be determined, either directly or when divided by the value 2 or 5 adopted for the constant *k* in Equation 5.

If a weight of sample between 200 and 500 mg. in any case gives a volume of gas too small to be measured with accuracy, it is of course possible to take a weight of sample 10 times as great as that indicated by the point on the mg. scale to which the mercury in *B* is adjusted at the end of the determination. The final result is then divided by 10 to give the true percentage of the constituent to be determined. Or we may halve or double the numerals of the scale on *B*, if found convenient, the values etched on the glass being replaced by others on gummed labels, since the constant *K* in Equation 2 is perfectly arbitrary. By this expedient it is always possible to reduce the constant *k* in Equation 5 to unity, and the instrument becomes direct-reading in the strictest sense of the word.

An interesting application of the instrument is in the determination of molecular weights by the Victor Meyer method. The correction-tube is filled with air as usual, giving the quantity *mM* in Equation 5 the value 100. The air expelled from the vapor-density apparatus by the vaporization of the substance whose molecular weight is to be determined is collected in the measuring tube *A*, the levelling tube *C* being lowered until the process is complete.

When the volume of air in *A* no longer increases, or even begins to decrease, *C* is adjusted again, and the stopcock at the top of *A* is closed. The vapor density apparatus is then disconnected and the mercury in *B* is brought to a mark corresponding to ten times the weight of sample taken. The molecular weight is then one thousand times the reciprocal of the volume of gas read from the measuring tube, and may be obtained instantly from a slide-rule or table. Even this calculation may be avoided if a small tube (about 30 cc.) graduated with a reciprocal scale like that of *B* for the range of molecular weights likely to be met in practice (Equation 3) is substituted for the tube *A*. In this case the constant *M* in Equation 5 is given the value $Z/10$, where *Z* is the volume of the substitute tube *A* (above any given point) multiplied by the value which has been assigned to that point in the arbitrary scale of weights inscribed on that tube. In this case the reading on that scale, at the moment the mercury in *B* has been compressed to a mark corresponding to ten times

the weight of the sample vaporized, will be the required molecular weight.

In carrying out molecular-weight determinations by this method, it is of course important that all connections be air-tight. Certain devices in use for dropping the sample make this difficult. The best method is to let the capsule containing the sample rest on an iron wire projecting from the delivery tube into the vertical stem of the vaporization tube. When all connections have been made tight and the pressure in the apparatus has been somewhat decreased by lowering C , the sample is dropped by moving the wire with a magnet.

Illustrative Results.

M. V. Del Rosario very kindly carried out a number of determinations with the instrument that has been described, and reports the following results:

Determination of Nitrogen in Potassium Nitrate:

Reaction carried out in tube A .

C. P. sample recrystallized and dried at 110° .

$T = 302.5^{\circ}$; $P = 762.5$ mm.; $k = 2$; $W' = 226.7$.

Results: 13.82%, 13.96%, 13.81%, 13.72%, 13.78%, av. 13.81%.

Calc. 13.75%.

Determination of Hydrogen Peroxide:

Commercial sample.

$T = 302^{\circ}$; $P = 764$ mm.; $m = 2$; $W' = 276.3$.

Results: 2.79%, 2.79%.

Duplicate determinations by titration with potassium permanganate solution, standardized with oxalic acid, gave 2.79%.

Determination of Carbon Dioxide in Calcium Carbonate:

C. P. reprecipitated sample, dried at 110° .

$T = 301^{\circ}$; $P = 764.5$ mm.; $m = 2$; $W' = 358.8$.

Results: 44.11%, 44.16%, 43.76%, av. 44.01%.

Calc. 44.00%.

Summary.

This paper describes a gas-volumeter in which a tube graduated in terms of the weight of sample has been substituted for the correction tube of the Lunge gas-volumeter. This instrument reads directly in percentages of any desired constituent, for any weight of sample, no matter what the nature of the substance analyzed.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,
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THE SURFACE TENSIONS OF THE CO-EXISTING LAYERS OF SYSTEMS OF MUTUALLY SOLUBLE LIQUIDS.

BY J. LIVINGSTON R. MORGAN AND WARD V. EVANS.

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The object of this investigation was to secure accurate data in regard to the surface tensions of the separate layers of some of those non-homo-