

methyl and ethyl alcohols. He found the degree of dissociation to be very nearly constant in both cases, and to have a value of about 50% in methyl alcohol and 25% in ethyl alcohol. This is exactly in accord with our values for the lowering of the vapor tension. The conductivity determinations of Zelinsky and Krapiw<sup>1</sup> showed substantially the same thing, although other observers<sup>2</sup> have found that the molecular conductivity increases with the dilution in very dilute solutions.

Why the calculated molecular weight should remain constant over such a range of concentrations is difficult to explain. It may have something to do with the combination of the salts with the solvents and to the progressive combination of the ions with the solvents. However, in such a case, one would not expect potassium iodide to be so subject to these effects as lithium chloride.<sup>3</sup> If, in plotting the curves, the values of  $n$ , in the fifth column, had been used as abscissas instead of the concentrations of the second column, all of the curves would be thrown closer together, and those of potassium iodide and lithium chloride in methyl alcohol would be almost superimposed, indicating almost identical molecular states.

As to benzil, its molecular weight in ethyl alcohol seems to be normal, while in methyl alcohol it seems to be associated with one or two molecules of the solvent.

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## A MODIFIED PRECISION BAROMETER.

BY ALBERT F. O. GERMANN.

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In the determination of the densities of gases by the various precision methods involving the measurement of volume, pressure, temperature, and mass,<sup>4</sup> the evaluation of the pressure is perhaps the most difficult, and the values obtained for this factor are always much less accurate than those obtained for the temperature, volume, and mass, particularly when the first two are taken at the temperature of melting ice, and the mass is taken as the average of the mass of several samples of gas simultaneously taken. A great many special barometers and manometers have been designed in an effort to eliminate the errors to which this type

<sup>1</sup> *Z. physik. Chem.*, **21**, 38 (1896).

<sup>2</sup> See Carrara, *Gazz. chim. ital.*, [1] **26**, 119 (1896); also Turner, *Am. Chem. J.*, **40**, 558 (1908).

<sup>3</sup> According to Turner and Bissett, *J. Chem. Soc.*, **103**, 1904 (1913), lithium chloride forms no compounds with methyl alcohol above 10°, but with ethyl alcohol LiCl·4C<sub>2</sub>H<sub>5</sub>OH exists up to a temperature of 17.4°.

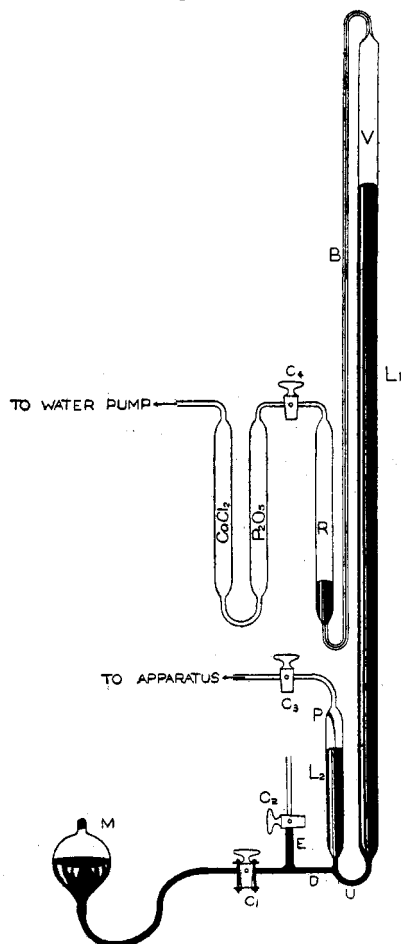
<sup>4</sup> See, for example, article by the author, *J. chim. phys.*, **12**, 66 (1914).

of instrument is subject, chief of which are the residual pressure in the barometric vacuum, and variations in the meniscus. Both objections would appear to be remedied in the barometer of wide bore, the vacuum chamber of which communicates with a mercury pump; here capillarity no longer exercises an appreciable influence; the meniscus, therefore, is perfectly flat, except at the edge; and the quality of the vacuum is under the experimenter's direct observations and control. But even here concordant readings cannot be obtained, because of various disturbing factors, such as non-uniformity of temperature, even when surrounded by an air bath, and the difficulty of getting a sharp reading of the position of a large mercury surface. Experience with this type of barometer has nevertheless demonstrated its superiority over the type composed of narrow tubing, where meniscus corrections must be made, and over the type sealed at the top, which may be expected to give low readings, unless filled while boiling the mercury and simultaneously making a vacuum with a good mercury pump. Barometers filled in this way, however, may not be successful, because a meniscus often fails to form in those portions of the barometer tube which have been heated to drive out air, due to some change in the glass. At the *École de Chimie* in Geneva, the author remembers seeing one barometer of this type stand for a week, without a suggestion of a meniscus; then one morning a perfect meniscus appeared, only to disappear after a day or two, never to appear again.

It would seem, then, that to secure the most uniform results, it would be imperative not to subject those portions of the barometer tube in which the mercury surfaces are to rest, to a high temperature. The barometer must, then, not be permanently sealed, so as to permit of the removal of the traces of air adhering to the glass, which are slowly given up under the decreased pressure. One device for doing this is to terminate the barometer with some form of stopcock<sup>1</sup> through which the accumulated air may be expelled; or the vacuum chamber may communicate with a mercury pump. The first method is open to the objection raised by Professor Morley against all stopcocks used in connection with a vacuum—a stopcock is usually nothing more than a located leak; the other method is expensive and more or less time-consuming, since each stroke of the pump removes only a definite fraction of the residual air in the barometer. This objection suggested to the author the combination of pump and barometer into one instrument; similar modifications have been described, but because of certain practical objections, have not been adopted in research laboratories. The type described below has met with approval in several European laboratories, and may be found useful in this country. A knowledge of the simpler operations of glassblowing is, of course, necessary for its construction.

<sup>1</sup> R. A. Baker, *THIS JOURNAL*, 35, 199 (1913).

The barometer (see figure) is really a modification of the mercury pump described by Cardoso and the author,<sup>1</sup> in which the main reservoir has been omitted. The two branches,  $L_1$  and  $L_2$ , are, as usual, cut from the same glass tube, and connected at the bottom by means of the narrow U-tube  $U$ . The short branch  $L_2$ , about 20 cm. long, has sealed into it at  $P$  a colored glass point, to which the lower mercury surface may be ad-



justed in making a reading; the gaseous pressure to be measured is admitted through the stopcock  $C_3$ . The U-tube has sealed into it at  $D$  a T-tube bearing the stopcocks  $C_1$  and  $C_2$ , each of which is lubricated with Acheson graphite, rather than with stopcock grease, to keep the mercury clean; since the graphite has no adhesive power, the stoppers are held in place by means of brass stopcock clamps; any air admitted with the mercury collects at  $E$ , and may be expelled through  $C_2$ . The other branch,  $L_1$ , which measures about 110 cm., terminates in a fine capillary tube  $B$ , about 76 cm. long and 0.2 mm. bore, bent down so as to rest against the barometer tube  $L_1$ ; the lower end of  $B$  is bent upwards and bears a wide tube  $R$ , which may be connected to the water pump via the stopcock  $C_4$  and the drying tubes containing  $P_2O_5$  and fused  $CaCl_2$ .

After careful cleansing with appropriate reagents, and rinsing with distilled water, the barometer should be dried by passing a slow current of dry air through it for a week; this insures the removal of traces of moisture

in the pores of the glass. Then the instrument may be mounted on a suitable support, against a graduated glass plate, and filled. To carry out this operation, stopcocks  $C_2$  and  $C_3$  are closed, and  $C_1$  and  $C_4$  opened. Freshly distilled mercury is poured into the reservoir  $M$ , which is connected to the barometer by means of a rubber tube, and gentle suction applied through the drying tubes and  $C_4$  by means of the water pump; or

<sup>1</sup> Germann and Cardoso, *J. chim. phys.*, 10, 306 (1912).

the water pump may be dispensed with at this point if the rubber tube be long enough to allow  $M$  to be raised to the top of the barometer. Mercury is allowed to completely fill the tube  $L_1$ , and to run over into the reservoir  $R$ , into which the air has been driven. Then the bulb  $M$  is lowered, the mercury in  $L_1$  subsides to a point at which it is in equilibrium with the air enclosed in  $L_2$ ; the level of the mercury in  $L_2$  may be adjusted to the glass point by opening the stopcock  $C_3$  and adjusting the height of the mercury bulb  $M$ ; the air admitted with the mercury, and which has collected at  $E$ , may be expelled through  $C_2$ . If the length of the capillary  $B$  has been properly adjusted, any great excess of mercury in  $R$  will be forced back into  $V$  by the pressure of the atmosphere;  $B$  must, however, not be shorter than the maximum local barometric height to prevent the totality of the mercury from being forced back with the resultant destruction of the vacuum.

After several days, a certain amount of air will have disengaged itself from the glass walls of  $V$ , and the barometer will consequently give too low a reading. This may be verified by lifting the bulb  $M$  until the mercury rises in  $V$ , and approaches the mercury thread in the capillary; the minute volume of air present prevents the mercury surfaces from meeting. The test is an extremely delicate one, because the air in question is under a very small pressure; and if an effort be made to expel it, it may adhere to the capillary walls of  $B$ , when the volume has been sufficiently reduced by the increasing pressure. To effect the expulsion of the air,<sup>1</sup> it then becomes necessary to make a partial vacuum in  $R$ , by turning on the water pump; the air bubble expands, and is forced out. A single operation of this kind always suffices to test the vacuum, and to get rid of the merest traces of gas.

While working on the densities of oxygen and air,<sup>2</sup> the author had an opportunity of comparing two barometers of the type described with two others whose vacua were controlled by means of a mercury pump; one of the latter served as standard, as its internal diameter was about 25 mm., and hence no meniscus corrections had to be made; the others had a diameter of approximately 15 mm. Corrections for capillarity were very small, but were nevertheless made, applying the following considerations, suggested by Ph. A. Guye.

<sup>1</sup> As a matter of fact, it may be readily shown that this small amount of gas may be left in the barometer without, in any appreciable way, affecting the barometric reading. Assuming the volume of  $V$  to be 35 cc., the diam. of the capillary 0.2 mm., and the length of the thread of air in the capillary 5 mm., under a pressure of, say, 5 cm. of mercury, a simple calculation will show that the pressure of this volume of air amounted, in the 35 cc., to approximately 0.00001 mm.

<sup>2</sup> *Compt. rend.*, 157, 926 (1913); *J. chim. phys.*, 12, 66 (1914); Germann, "Geneva Thesis," No. 514.

Laplace<sup>1</sup> has shown that

$$p = A \left( \frac{1}{R} + \frac{1}{R'} \right)$$

where  $A$  is the capillary constant and  $p$  the pressure in mm. of water due to the capillary action in various directions of a liquid surface, whose principal radii of curvature are  $R$  and  $R'$ . For practical purposes, we may consider that  $R$  and  $R'$  are equal; then

$$p = \frac{2A}{R}$$

Laplace found by experiment for mercury  $A = 44.07$ ; Desains found  $A = 45.97$ ; using the mean of these values, we have for  $p$ , expressed in mm. of mercury:

$$p = \frac{2 \times 45}{13.56} \frac{1}{R} = \frac{C}{R}$$

where  $C$  is a constant equal to 6.6.

Besides this, the following corrections were applied:

- (a) for the thermal expansion of mercury
- (b) for the thermal expansion of the glass scale
- (c) for altitude and latitude, *i. e.*, for gravity

Combining (a) and (b) into a single correction, which we will denote by  $\tau$ , and denoting the correction for gravity by  $G_o$ , we have the expression for the corrected barometric height:

$$H = G_o(h + p_s - p_i - \tau)$$

where  $h$  is the uncorrected distance between the lower edge of the two menisci;  $p_s$  the pressure exercised by the upper meniscus, and  $p_i$  that exercised by the lower meniscus; but

$$p_s - p_i = c \left( \frac{1}{R_s} - \frac{1}{R_i} \right)$$

whence

$$H = G_o \left[ h + c \left( \frac{1}{R_s} - \frac{1}{R_i} \right) - \tau \right]$$

The value of  $1/R$  varies with the height,  $f$ , of the meniscus and becomes approximately equal to zero with a flat meniscus, when it becomes superfluous to read the lower edge; this was the case with the 25 mm. barometer.

To facilitate the calculation of  $c(1/R_s - 1/R_i)$ , a curve was prepared for each barometer plotting as ordinates the possible meniscus heights, and the corresponding values of  $1/R$  as abscissas: knowing the height,  $f$ , of the meniscus, the value of  $1/R$  may be read directly from the curve. To construct the curves, the following method may be employed: A number of concentric arcs are constructed on millimeter paper; in each a

<sup>1</sup> *Annuaire du Bureau des Longitudes*, Paris, 1912, p. 533.

chord is drawn equal in length to the internal diameter of the barometer for which the curve is to serve; the length of the mid-ordinate<sup>1</sup> of the arc subtended by the chord gives the value of  $f$ , and from the radius  $R$  of the arc the corresponding value of  $1/R$  may be calculated.

The value of  $\tau$ , correction for the thermal expansion of mercury and glass scale, may be taken from any table of physical constants.

The gravity correction  $G_o$  is here taken, not as an additive correction, as is customary, but as a fractional one, for the sake of simplicity. Its value is the ratio of the normal acceleration due to gravity  $g_n$  (at sea level and  $45^\circ$  N. latitude) to the acceleration due to gravity at the place of measurement,  $g_m$ . For Geneva this ratio becomes<sup>2</sup>

$$G_o = \frac{g_n}{g_m} = \frac{980.616}{980.599} = 1.000017$$

which is a positive correction of approximately 2 in 100,000, a negligible quantity.

Table I contains the data obtained in two sets of readings with these barometers, being the values obtained in the course of two series of determinations of the density of air in Geneva. No. I is the standard 25 mm. barometer; II is one similar to it, having a diameter of 13.5 mm. III and IV are of the type described above, each of 15 mm. internal diameter. The values of  $h$  given are the averages of several readings;  $t^\circ$  is the average of the temperatures shown by four carefully checked thermometers, placed at various points along the mercury column.

TABLE I.

Series.	No.	$h$ .	$t^\circ$ .	$\tau$ .	$f_s$ .	$f_i$ .	$c\left(\frac{1}{R_s} - \frac{1}{R_i}\right)$ .	$H$ .
VII.....	I	764.9	16.5	2.18	..	..	..	762.72
VII.....	II	764.95	16.35	2.16	1.25	1.30	-0.01	762.78
VII.....	III	764.8	16.45	2.17	1.00	0.90	+0.02	762.65
VII.....	IV	764.9	16.4	2.17	1.00	1.00	..	762.73
VIII.....	I	762.8	15.6	2.06	..	..	..	760.74
VIII.....	II	762.7	15.5	2.04	1.30	1.25	+0.01	760.67
VIII.....	III	762.7	15.5	2.04	1.10	1.00	+0.02	760.68
VIII.....	IV	762.85	15.6	2.06	1.05	1.00	+0.01	760.80

This plainly demonstrates the dependability of the pressure readings obtained with barometers III and IV. At the same time it shows the impossibility of getting as concordant results as, for example, in the determination of volumes, where it is possible for different experimenters to check each other to within one part in thirty or forty thousand, without any very great precautions. Obviously, too, a much higher degree of

<sup>1</sup> In the sense in which the term is used in surveying, *viz.*, the outer segment of a radius cut by a perpendicular chord.

<sup>2</sup> *Recueil de Constantes Physiques*, 1913, pp. 93 and 96.

accuracy in the determinations of gaseous pressures may be obtained by the simultaneous use, as above, of several good barometers.

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## A QUALITATIVE TEST FOR WATER BY THE USE OF THE ACETYLENE-CUPROUS CHLORIDE REACTION.<sup>1</sup>

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### CONTENTS.

Outline of method and previous related work. (a) Preparation of Reagents: Anhydrous Solvents; Cuprous Salt Solutions; Removal of Acetylene from Calcium Carbide. (b) Methods of Making Test: Blank Tests. (c) Compounds Interfering with Test: Action of Acids; Tests of Oleic Acid and Glycerol. (d) Sensitiveness of Test. (e) Summary.

In the course of the examination of certain carefully purified organic compounds<sup>2</sup> it was found that a simple, quick and very delicate qualitative test for water, showing approximately the amount present, can be made in the following manner: The substance under examination is placed in contact with calcium carbide in the presence of a solvent for acetylene, and any acetylene formed by the action of water is detected by adding the resultant solution to an ammoniacal solution of cuprous chloride. The following paper describes the application of this method simply as a qualitative test for water. A large amount of work has already been done with a view to applying the acetylene-cuprous chloride reaction to the quantitative determination of both water and acetylene, and a colorimetric method for acetylene depending upon the formation of copper carbide in a colloidal form has been devised. The publication of this work is planned for the near future.

Calcium carbide has recently been quite extensively used for the determination of water in substances which, for any reason, do not permit the application of the more usual methods of analysis. It was suggested by Berthelot,<sup>3</sup> that the acetylene evolved in the reaction could be determined by absorption in an ammoniacal solution of a silver salt with subsequent titration of the excess of silver. This method was tried by Rivett<sup>4</sup> for the determination of water in butter, but was not successful on account of the incomplete absorption of the evolved acetylene. With this exception, all the chemists who have used the calcium carbide method seem to have determined the evolved acetylene either volumetrically or by loss in weight. Obviously, neither of these methods is applicable to

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

<sup>2</sup> THIS JOURNAL, 35, 1309 (1913).

<sup>3</sup> *Compt. rend.*, 129, 361 (1899).

<sup>4</sup> *Chem. News*, 104, 261 (1911).