tained; because failure to realize this possibility has been a chief cause of inconsistences in all measurements by the static method.

As, therefore, it seemed of interest to determin whether any small difference could be detected between static and dynamic results, the experiment was made with pure water, alcohol and benzene. The following figures refer to benzene, which had recently been distilled over sodium, but was not boiled out in the jacket. The differences of pressure, Δp, are in mm. of benzene at its boiling point, while the times, T, refer to the number of minutes of the "blowing-through" process:

Δp..................	6.3	2.5	0.9	0.1	0.1
T....................	5.0	6.0	8.0	10.0	12.0

The zero reading was that found when the stopper was removed. It will be seen that the difference of pressure finally observed was not larger than the limits of the error of observation.

It was shown in a similar way that, if any difference exists between the vapor pressure at the boiling point as measured dynamically and statically of the liquids water and alcohol, then such difference does not exceed 0.01 mm. of mercury.

Purpose and Scope.—In the present paper, the purpose has been to describe a molecular weight apparatus and its every-day application in cases where the greatest refinement is not aimed at. When opportunity offers, it is proposed to carry the measurements to their highest accuracy, and to make such applications of the method as promise to be most productive.

[COMMUNICATIONS FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

A CONVENIENT FORM OF APPARATUS FOR THE MEASUREMENT OF THE VAPOR DENSITIES OF EASILY VOLATIL SUBSTANCES.[1]

BY ALAN W. C. MENZIES.

Received October 26, 1910.

By the very slight modification here explained, the apparatus described in the preceding paper may be simply adapted for the rapid and accurate measurement of vapor densities of easily volatil substances.

The principle employed is that of the measurement of the increase of pressure that occurs when a known weight of substance is introduced into a closed vessel at constant temperature, high enough to completely volatilize the substance.[2]

The Modification Required.—The closed chamber is provided by

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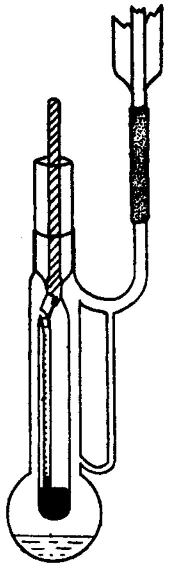
[1] Read before the American Chemical Society, July 15, 1910.

[2] For other work in this field cf. Gibson Dyson, *Chem. News*, 55, 88 (1887); Bleier and Kohn, *Monatsh.*, 20, 909; 21, 575; Lumsden, *J. Chem. Soc.*, 83, 342; Blackman, *Chem. News*, 100, 13; etc.

the "test-tube" of the former apparatus, which is the inner tube in the figure. This is closed below by pouring in from six to eight cc. of mercury. This mercury serves at the same time the purpose of manometer liquid, indicating by its rise in the graduated narrow gage tube the increase of pressure within the test tube.



The substance is weighed off in bulblets whose attached capillaries, 2–3 cm. in length, are sealed off before the final weighing. In order to attach the bulblet to the stopper of the test tube, the latter must be provided with a hole of about 1.5 mm. diameter and 5–6 mm. length. This hole may be drilled in the glass stopper, or else *added* by fusing to the lower end of the stopper a short length of thick-walled tubing of 1.5 mm. bore. The point of the bulblet's capillary can now be fixed in this hole by stuffing with a few shreds of dry asbestos. The hole should be oblique, in order that the neck of the bulblet may be broken by rotating the stopper in such a way that the bulblet is forced against the top of the gage tube (see figure). It is evident that the presence of this small hole in no wise unfits the apparatus[1] for its original purpose.

The Procedure.—The bulb of the outer jacket is charged one-third full with a liquid of suitably high boiling point, which is caused to boil steadily, the vapor thus serving to jacket the whole of the closed portion of the test tube. It is most convenient in practice to find a constant for the apparatus, at the temperature used, by volatilizing a known weight of a standard liquid, such as benzene, rather than to calculate the vapor density from measurements of the volume of the closed chamber and of the temperature. A quantity of benzene suitable to give a rise of mercury level of about 100 mm. is, therefore, sealed and weighed in a bulblet. The smaller the bulblet that will hold the requisite quantity of liquid, the better. The neck of the bulblet is then prepared for easy breaking by one or two scratches from a file. The tip of the capillary is inserted in the hole in the stopper, and the latter, after suitable lubrication, placed cautiously in its position. As the air surrounding the cold bulblet becomes warmed, the mercury rises a few mm. in the gage tube and in 5–6 minutes has reached a constant level, which is read off on the engraved scale of mm. Its position is shown in the figure. The stopper is now rotated so as to snap the neck of the bulblet, which falls on to the surface of the mercury. At the same instant the mercury in the gage

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[1] The apparatus, with the modified stopper, may be had from the Central Scientific Co., 349 W. Michigan Street, Chicago, Ill.

tube shoots up, and reaches a constant level in a few seconds. The amount of rise is observed, and is corrected by adding the amount of the simultaneous slight fall of mercury level in the test tube.[1] From the three data (1) weight of benzene taken, (2) known molecular weight of benzene, (3) rise in mm., is calculated a constant for the apparatus, K, which is the rise in mm. that would be caused by the volatilization of one gram-molecular weight of any substance in this apparatus at this temperature. Having obtained this constant, the unknown molecular weight of any substance may be calculated by substituting the measured rise, R, and weight taken, W, in the formula

$$M = W \cdot K/R.$$

After each measurement, the stopper is removed and a current of air aspirated through the test tube for a few seconds by introducing into it the end of a tube connected with the water pump. Several of the broken bulblets may be allowed to accumulate in the apparatus.

Examples of Results.—The measurements recorded below, including the time necessary for the weighings and for finding the constant of the apparatus, were completed in a period of three hours. The jacket contained boiling toluene. The substances whose molecular weights are determined were the preparations of Kahlbaum, each dried and purified by distillation. The chloroform was previously freed from alcohol by washing with chromic acid mixture. Every result obtained is given:

Substance.	Weight taken.	Rise in mm.	Log. K.	Molecular weight. Found.	Molecular weight. Normal.
Benzene	0.0238	16.5	5.5820	....	78.05
	0.0205	100.5	5.5827	....	....
Ethyl iodide	0.0429	104.7	5.5824	156.7	156.0
	0.0328	80.5	....	155.8	....
Carbon disulphide	0.0262	132.1	....	75.8	76.1
	0.0180	90.7	....	75.9	....
Chloroform	0.0312	99.9	....	119.4	119.4
	0.0347	110.0	....	120.6	....
Methyl iodide	0.0328	87.4	....	143.6	141.9

For the following determinations, I am indebted to Mr. R. D. Mullinix, who was without previous experience of vapor density measurements by any method, and who, indeed, first learned to weigh accurately in order to make these determinations. The jacket contained commercial xylene, b. p. 137.8°. Every determination made by Mr. Mullinix, other than his preliminary ones, is recorded:

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[1] The value of this correction for a given rise of mercury in the gage tube having been determined once, the values for other cases are thereafter obtained by simple proportion.

Substance.	Weight taken.	Rise in mm.	Log. *K*.	Molecular weight.	
				Found.	Normal.
Benzene	0.0215	112.0	5.6091	...	78.05
	0.0210	110.3	5.6126	...	...
	0.0211	110.1	5.6098	...	...
Toluene	0.0246	110.2	5.6105	91.1	92.1
	0.0231	100.2	....	93.2	
	0.0248	108.0	....	93.6	
Acetone	0.0158	108.1	....	59.6	58.0
	0.0157	108.9	....	58.9	...
	0.0156	113.8	....	55.9	...
Chlorobenzene	0.0276	100.1	....	112.4	112.5
	0.0270	95.5	....	115.3	...
	0.0266	89.1	....	121.8[1]	...
Ethyl iodide	0.0418	108.6	....	157.0	156.0
	0.0409	107.1	....	155.7	...
	0.0433	not completed—stopper leaked			...
Pyridine	0.0216	108.9	....	80.9	79.0
	0.0238	124.0	....	78.2	...
	0.0233	120.7	....	78.5	...
Acetic acid[2]	0.0140	92.6	....	61.7	60.0
	0.0162	106.7	....	61.9	

As an example of the application of this apparatus to a special problem, the percentage composition of a binary mixture of substances of known molecular weight may be found. For this purpose, the solubility of carbon disulphide in methyl alcohol was determined at 22.2°. The average molecular weight of the upper layer obtained on mixing these liquids was found to be 52.5, which would give a percentage of carbon disulphide of 53.4. Interpolation from the data of Rothmund[3] would lead to 52.3. In cases of this kind, other analytical methods are sometimes troublesome.

Remarks on the Method.—The apparatus is considerably more compact than the Victor Meyer form, and stands at a convenient level above the working bench. It is very simply set up, requiring a single ring stand with two clamps, one of which holds the condenser.

If a constant be determined as suggested, correction is, of course, not necessary for the density of mercury or for its vapor pressure. If a record be kept of the volume of mercury employed, the constant need not be redetermined when the apparatus is next used.

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[1] At normal pressure, chlorobenzene boils at 132°. The temperature of the jacket was 137.8°. As the pressure within the closed chamber increases, the volatilization of the chlorobenzene from the bulblet becomes rather slow.

[2] It will be seen that the values obtained for acetic acid, whose vapor is known to be associated, differ little from the monomolecular value. It must be recalled that, in this apparatus, the partial pressure of acetic acid vapor in the closed chamber is less than one-seventh of an atmosphere.

[3] *Z. physik. Chem.*, 26, 475.

Correction for change of jacket temperature due to barometric change is negligible. Thus, 23 mm. change of barometer causes a change of 1° in the boiling point of toluene (384° absolute), or 1 part in 384 in the result.

When the final level of the mercury in the gage tube is very different from that measured in finding the constant of the apparatus, it is plain that the gas content of the test tube will be somewhat different. Correction for this is usually unnecessary, and was not made in the above examples.

As every portion of the enclosed chamber is kept at the constant high temperature, there is nothing to be feared from the diffusion of the vapor to colder parts of the apparatus, as in the case of the Lumsden or Victor Meyer apparatus. Thus, Lumsden remarks:[1] "The accuracy of the results depends very much on the rapidity with which the substance is vaporized, and this is the more important the smaller the molecular weight, since a vapor which diffuses rapidly may reach the colder part of the apparatus before a measurement of pressure can be made." Again, as no air is driven from a hotter to a colder place, no uncertain correction on this account has to be considered.[2]

Since the vapor is likely to be diffused throughout the whole of the test tube, and since the pressure read is less than one-sixth of an atmosphere, the partial pressure of the vapor cannot even locally much exceed one-sixth of an atmosphere. This low pressure lessens any tendency to association, as is seen in the acetic acid example given above. It is obvious that the test tube may be filled with an inert gas if desired.

Instead of a glass stopper, a one-holed rubber cork may be used at the lower temperatures. A glass rod, bent for the lowest centimeter of its length, passes through the hole, and by its timely rotation breaks the neck of the bulblet, which is inserted into a small blind hole beside it, and is pressed against the top of the gage tube. This form of "release" is perhaps easier to operate than that described above.

In the form described, this apparatus is not suitable for temperatures above 200°; but the examples given seem to show that it is both rapid and accurate for use at temperatures at which it is applicable.

RAPID DETERMINATIONS AND SEPARATIONS BY MEANS OF THE MERCURY CATHODE AND STATIONARY ANODE.

By R. C. Benner and M. L. Hartmann.

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The mercury cathode has been used for most metals which can be determined electrolytically. In the case of bismuth it is possible to make

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[1] *Loc. cit.*

[2] Cf. T. W. Richards, *Chem. News*, 59, 87.