determined with a fair degree of accuracy we have collected the results in Table XX.

TABLE XX.

Compound.	M. P.
$(CH_3)_2O.HBr$	— 13°
$(CH_3)_2O.HI$	— 22°
$(CH_3)_2O.HCl$	— 96°
$(CH_3)_2O(HCl)_3$?	—102°
$CH_3HO.HBr$	— 12°
$CH_3HO.Br$	— 66°
$C_2H_5HO.HBr$	— 30°
$C_2H_5HO.Br$	— 58°
$C_3H_6O.HBr$	— 4°
$C_3H_6O.Br_2$	— 8°
$C_3H_6O.Cl_2$	— 54°
$CH_3COOC_2H_5.HBr$	— 36°
$(CH_3COOC_2H_5)_2(HBr)_5$	— 52°
$(CH_3COOC_2H_5)(HBr)_4$	— 57°
$CH_3COOC_2H_5.Br_3$	— 35°
$CH_3COOC_2H_5.Cl_3$	— 68°

In these compounds we believe that the union is brought about by the increase in valency of the oxygen at the low temperatures employed. The halogen hydride complexes, it will be noticed, melt far above the melting points of either constituent. The combinations are formed with the evolution of an amount of heat equal to or greater than that given out when a halogen acid is neutralized by potassium hydroxide. These compounds whether molten or in a solution of either constituent conduct the electric current readily.

The chlorine and bromine compounds evolve only a small amount of heat on their formation, and are non-conductors when free from the corresponding halogen acids. Their constitutional formulas are doubtful, but they must differ radically from the compounds ionized in solution. We are now attempting to solve the question of their structure and that of other oxonium and carbonium complexes by means of molecular weight determinations at low temperature.

McGILL UNIVERSITY, July, 1912.

A METHOD FOR DETERMINING THE MOLECULAR WEIGHTS OF VOLATIL LIQUIDS.

BY C. W. PORTER.

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All vapor density methods for determining molecular weights are based upon the gas law as expressed in the equation $PV = RT$. The numerical value of the constant (R) is usually calculated by allowing P to represent atmospheric pressure at sea level, T, 0° C. (273° Abs.) and V the volume occupied by a gram molecule of a gas under the above conditions of temperature and pressure. If more or less than a gram molecule of a gas or vapor be under consideration an additional factor (n) is introduced to avoid the necessity of changing the value of R. The general expression of the gas law then becomes $PV = nRT$. Now since n is the number of molecules or the fractional part of a molecule employed its value may be represented by W/M in which W is the weight of substance used and M is the molecular weight. Substituting this value for n we have $PV = WRT/M$ or $M = WRT/PV$. In this equation R is constant but W, T, P and V are variable quantities. It is evident that if any three of these variables be fixed in value, by the condition of the experiment, the value of M may be calculated from a measurement of the fourth variable. Thus in the Victor Meyer[1] method a weighed quantity of the substance is volatilized at a fixed temperature and pressure and V is the variable determined by measurement. This same principle is applied in the Gay-Lussac[2] and Hofmann[3] methods. In the Gibson-Dyson method and also the Menzies[4] method a weighed quantity of substance is volatilized at a fixed temperature and is confined in a known volume; W, T and V are fixed by the conditions of the experiment, P is the variable measured. Dumas[5] filled a bulb of known volume at a fixed temperature and pressure then determined the weight of vapor in the bulb. In his work, P, V and T were fixed while W was the factor to be measured.

There is just one other possible application of the gas law to vapor density measurement, *viz.*, a method in which P, V and W are fixed and T is the factor to be determined. This was accomplished by the following method which was suggested to the writer by Prof. T. W. Richards, of Harvard University. A glass bulb, *A*, having a capacity of about 300 cc. is immersed in a glycerol and water bath contained in a large glass jar tubulated near the bottom. A tube of small bore is sealed on each end of the bulb. One of the tubes passes through a one hole stopper in the tubulature of the jar, and is connected by means of a thick-walled rubber tube to a mercury reservoir, *B*. The tube at the upper end of the bulb connects at *C* with a short capillary tube; and the capillary is, in turn, sealed by a solid glass plug and rubber connection at *D*. The glycerol bath is heated by a current of electricity through coils of nichrome wire, *W*. The volume of the bulb from the plug at the top to a file mark at *E* on the tube at the bottom is accurately determined. Mercury is poured into the reservoir *B* until the level in the tube stands at *E*. The bulb is then completely filled with mercury by pressure applied at *P* by means of an air pump. Before the mercury reaches the top of the

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[1] *Ber.*, 11, 2253.

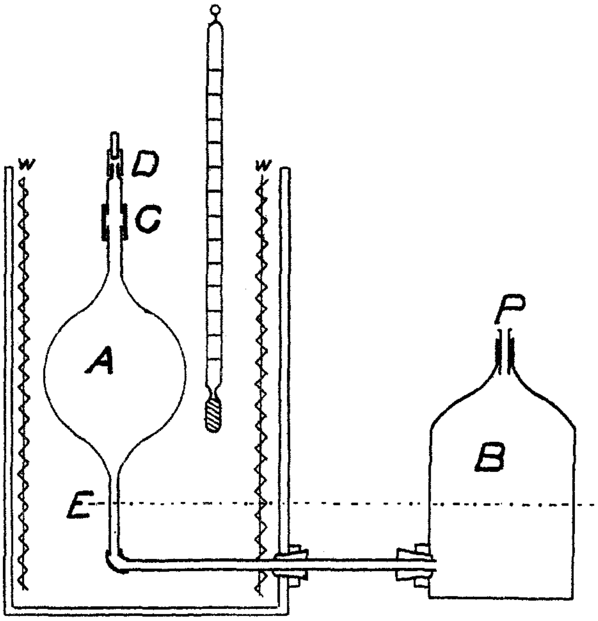
[2] Biot, *Traité*, 1, 291.

[3] *Ber.*, 1, 198; 9, 1304.

[4] THIS JOURNAL, 32, 1625.

[5] *Ann. chim. phys.*, 33, 337 (1826).

tube a small glass bulb containing a weighed sample of the liquid to be investigated is dropped on the surface of the mercury in such a way that the long capillary end of the bulb will be directed upward. The tube *C* is then placed in position, held by a heavy rubber tube and securely wired. Pressure is then applied until a drop of mercury appears at the top of the capillary at *D*. The plug *D* is then inserted and the rubber connection wired. The mercury has now forced the end of the bulb containing the weighed liquid into the capillary bore of *C*. By bending the connection at *C* slightly, the end of the small bulb is broken off and vapor from the liquid is free to escape. The bath is then gently heated and vigorously stirred. When the mercury has been forced down to *E* it is at the same level as that in the reservoir, and the vapor is under atmospheric pressure. A thermometer in the bath indicates the temperature. The heating is continued until the level is a little lower; then the system is allowed to cool slowly and the temperature again read when the level is at *E*. When the rising and falling column reaches *E* at a temperature that is constant within half a degree the reading is recorded. The volume of the bulb must be corrected for the temperature attained, and the vapor tension of mercury at the observed temperature must be subtracted from the barometic pressure before the calculation of molecular weight is made. In the following table the volume correction is made for the bulb, but in the column headed barom. (corr.) the



barometric reading has been corrected only for the temperature of the barometer and not for the vapor tension of mercury.

The following measurements have been made by this method:

Wt. of sample.	Temp. of bath.	Vol. of bulb at temp. of bath.	Barom. (corr.).	Mol. wt. found.
		Acetone.		
0.4618	75	265.36	640.3	59.02
0.4520	81.5	265.40	640.4	58.82
0.4710	67.5	265.30	639.8	58.94
0.4410	95	265.50	640.9	59.53
0.4675	64.5	265.28	640.9	57.86
0.4655	73.5	265.34	640.9	59.17
		Ether.		
0.5638	93	265.48	640.4	75.75
0.6060	90	290.90	640.0	73.98
0.6194	82.5	290.80	640.0	73.83
0.6303	86	302.68	640.5	72.83
0.6474	96.4	302.76	640.2	77.04
0.6556	92	302.75	640.4	77.05
0.6570	88	302.71	640.7	76.32
		Benzene.		
0.6507	100	302.80	640.7	78.10
0.6337	110	302.87	640.7	78.13
0.6288	112.8	302.90	640.7	78.10
		Toluene.		
0.6389	128	265.71	642.4	93.90
0.7013	115	265.63	640.9	99.89
0.7003	110	265.59	640.9	98.43

The toluene used in these experiments was Kahlbaum's subjected to one distillation. No further purification was attempted. The benzene was freed from thiophene by shaking with sulfuric acid, and was subsequently distilled over sodium. It was further purified by crystallization and a sample obtained that melted at 5.4° and boiled at 74.9°. (In this laboratory barom. = 640 mm.) The ether was freed from alcohol by shaking with water, then dried over anhydrous calcium chloride, filtered and distilled. The middle portion of the distillate passed over at a constant temperature and was used for these determinations. The acetone was purified by fractional distillation only.

No superiority over the Victor Meyer method is claimed for this plan. It is as convenient as most of the vapor density methods of determining molecular weights, and yields results as accurate as the writer has been able to secure by the older processes. Moreover, it completes the possibilities for molecular weight determinations under the gas law.

LOGAN, UTAH, July 1, 1912.