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"Sitzungsberichte der Mathematisch-physikalischen Classe." 1876; 2 copies for 1877; 2 copies for 1878.

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E. WALLER, PH. D.
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A REVIEW OF THE LATEST INVESTIGATIONS ON THE DISSOCIATION OF THE ELEMENTS AT HIGH TEMPERATURES.

BY H. ENDEMANN, PH. D.

Literature.—VICTOR MEYER and CARL MEYER: On a method of determining the vapor density.* *Berichte der deutschen chemischen Gesellschaft*, 11, 1867.

Method of determining the vapor density of substances which boil at temperatures above 440° C., and of such, which would corrode mercury or Wood's metal. Ibid., 11, 2253.

On the behavior of chlorine at high temperatures. Ibid., 12, 1426.

Prof. V. Meyer describes in the first article, mentioned above, an apparatus which he had in use for more than one year, for determinations of vapor density, and which would have been described sooner if the results had been accurate enough to generally recommend it for such delicate work. The idea which led him to construct this apparatus, was based on his desire to obtain a method by which the vapor density of even those substances could be determined, which would corrode mercury or Wood's metal. The cause of the inaccuracy of the results obtained with his first apparatus, was finally found and remedied, so that, in its present shape, the results will compare in accuracy with those obtained by other methods, while the method, in itself, is so simple, that it hardly requires more time and skill than an ordinary boiling point determination. He describes his apparatus and the mode of using it, as follows:

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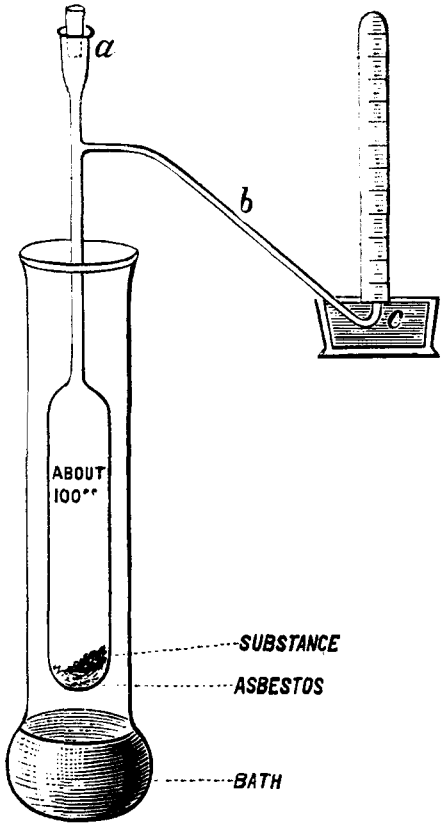
* The apparatus described here, may be obtained from Hrn. Glasblaeser Cramer, Zürich, Zwitzerland.

Supposing we have a vessel of the shape given in the accompanying figure, and of about 100 cc contents, which can be closed at *a* with a rubber stopper, which is always driven in to a certain mark—and this vessel heated by inserting it into the vapors of a boiling liquid, or into a bath of metal. if examinations are to be made at very high temperatures, it will be observed that after some time a constant temperature is reached. No air will thenceforth pass through *b*, which can easily be seen when its exit *c* is put under water. This point reached, a certain quantity of the substance is introduced through *a* after the stopper has been removed. The stopper is then at once replaced, and the vapor, which is formed if the temperature is high enough, will then cause a certain quantity of air to pass through *bc* into the graduated tube, placed for its reception, and wherein it is measured.



In order that the vessel containing the weighed portion of the substance shall not injure the apparatus in its descent, some asbestos or sand is kept at the bottom of the latter.

If the quantity of substance is so small that the vapor formed will fill only the lower part of the vessel (about $\frac{1}{4}$ to $\frac{1}{3}$), and if the vaporization takes but little time, the error caused by diffusion is but trifling. Also the circumstance that, as late investigations prove, the volume of two gases which do not act on each other chemically, is not equal to the sum of the separate volumes, causes only an error too trifling to prejudice the method for the determination

of molecular weights. That this is really the case, is proven by a series of experiments made by Mr. J. Qüblin and the authors—

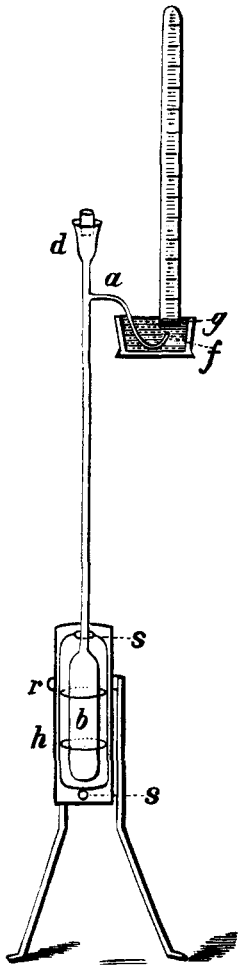
	Bath consists of boiling	Theory.	Found.
Chloroform	Water.....	4.13	4.32; 4.51; 4.44; 4.34; 4.40; 4.38; 4.36
Carbon disulphide	Water.....	2.63	2.87; 2.91; 2.92
Chloroform	Aniline.....	4.13	4.31
Water	Aniline.....	0.62	0.69; 0.66; 0.62
Xylole	Aniline.....	3.66	3.87; 3.83
Brombenzole	Aniline.....	5.43	5.11; 5.77; 5.59; 5.13; 5.00
Aniline	Ethyl benzoate.	3.21	3.27; 3.37
Aniline	Amyl benzoate.	3.21	3.29
Cymole	Ethyl benzoate.	4.63	4.75
Phenole	Ethyl benzoate.	3.25	3.28; 2.98

A peculiarity of the method just described, is that neither the contents of the vessel nor the temperature at which the experiment is made, need be known, since the volume of the vapor is measured in the form of an equal volume of air at the temperature of the laboratory. All that need be known is the temperature of the laboratory, the weight of the substance employed, the height of the barometer, and the volume of the air which has passed into the graduated tube. The vapor density of substances of very high boiling points may, therefore, be determined by this method at a very high, and unknown, temperature.

The following figure shows the construction of the apparatus as it is used for determinations at very high temperatures, or, generally, temperatures above 310° C., when a bath of lead is used for heating. The metal is contained in a wide wrought-iron gas pipe, 240 mm high and 60 mm wide, closed at the bottom, and held by a ring, to which feet are fastened which keep the bottom of the bath 320 mm above the floor. Each foot has a diameter of about 12 mm. The metal bath is heated by means of one or two gas burners to a temperature which need not be exactly known, but which should be high enough for the complete volatilization of the substance. Whether this temperature has been reached, is easily determined by immersing a thin test-tube, containing some of the substance, into the bath, and observing whether its contents boil briskly. At the same time it may be observed, whether perhaps the temperature be not too high and apt to cause decomposition.

The experiment is begun by bringing the vessel *b* into the bath and, if it be a lead bath, using a wire stay *s* to secure it against breakage by keeping it off the iron sides of the bath. The opening at *d* is closed by an india-rubber stopper.

The exit tube is chosen as small as possible, as the air inside causes a constant error, which is diminished with the degree of its diameter. It ends under water. As soon as the air ceases to pass off at *f*, which will be the case when the temperature has become constant, the rubber stopper is removed, and the tube containing the weighed portion of the substance is introduced at *d*, which is at once closed again with the stopper. From 1 to 2 air bubbles pass then into the water and are allowed to escape, as they are caused by the driving in of the stopper. But as soon as they have escaped, a graduated tube filled with water is put over *f*.



The volatilization commences in about ¼ minute after the introduction of the substance, and shows itself by the appearance of a constant stream of air bubbles passing into the measuring tube. As soon as the evolution of air ceases, the stopper is removed and the measuring tube is transferred into a wider one, wherein the inner and outer level of the water may be equalized, for the sake of avoiding unnecessary calculations.

Then the volume of the air V, the temperature of the water t, and the height of the barometer B (calculated for 0° C.), are noted, and from these and the known weight S of the substance, the density D is calculated by the following formula :

$$D=\frac{S.760\ (1+0.003665\ t)}{(B-w)\ V.0.001293}\ \text{or}$$

$$D=\frac{S(1+0.003665\ t).587780}{(B-w)\ V}$$

wherein w is the tension of aqueous vapor at the temperature t.

It is best to place the apparatus upon the floor, its dimensions being such that the pneumatic trough will then be at the height of an ordinary table. Substances which were acted upon by oxygen, must be tested in an atmosphere of nitrogen. For this end a current of nitrogen is passed through a tube reaching to the bottom of the apparatus to the complete expulsion of the air. The nitrogen may

be made by boiling a solution of 1 pt. potassium bichromate, 1 pt. ammonium nitrate and 1 pt. sodium nitrite, in 3 pts. of water, and passing the gas over a layer of red hot copper.

The authors give the following results which have been attained with their improved apparatus :

A.—Experiments in the vapor of boiling liquids.

	Substance in bath.	S	t	B	V	Density Calculated.	Found.
Chloroform	Water	0.1008	16°.5	707.5 mm	22.1 cc	4.13	4.13
Carb. disulphide	Water	0.0495	16°.5	717.8 "	16.4 "	2.62	2.68
Water	Xylole	0.0102	16°.1	723.3 "	14.6 "	0.62	0.61
The same	Xylole	0.0130	15°.4	723.8 "	17.8 "	0.62	0.64
The same	Xylole	0.0110	16°.0	724.3 "	15.2 "	0.62	0.63
Bromobenzole	Aniline	0.0975	15°.0	718.8 "	15.8 "	5.43	5.42
Xylole	Aniline	0.0715	16°.0	723.8 "	16.5 "	3.66	3.79
Phenole	Ethyl benzoate	0.0692	17°.0	718.3 "	18.2 "	3.25	3.38
Aniline	Amyl benzoate	0.0805	15°.5	722.3 "	21.3 "	3.21	3.31
Iodine	Amyl benzoate	0.1157	16°.1	722.3 "	11.6 "	8.78	8.75
The same	Amyl benzoate	0.1105	16°.0	714.8 "	11.1 "	8.78	8.83
Naphthaline	Amyl benzoate	0.0685	15°.0	723.8 "	13.2 "	4.43	4.52
Benzoic acid	Diphenylamine	0.0855	16°.0	717.8 "	17.8 "	4.22	4.24

B.—Experiments in the lead bath at unknown temperature.

Diphenylamine		0.0905	17°.0	714.8 mm	13.6 cc	5.84	5.92
The same		0.0990	18°.0	717.8 "	14.9 "	5.84	5.94
*Mercury		0.0905	16°.0	715.8 "	11.5 "	6.91	6.97
Anthracene		0.0530	17°.2	720.8 "	7.8 "	6.15	6.01
Anthrachinone		0.0730	18°.0	720.8 "	9.2 "	7.19	7.05
Chrysene		0.1125	15°.0	716.8 "	12.2 "	7.89	8.12
*Sulphur		0.1030	16°.0	713.8 "	13.9 "	6.63	6.58
Perchlordiphenyl		0.2270	15°.6	716.3 "	11.5 "	17.24	17.43

The applicability of this apparatus for all temperatures, is limited by the nature of the material from which it is constructed. For the highest temperatures, glass had to be abandoned and porcelain vessels were employed in its stead. In order to determine whether the method would hold good at very high temperatures, such as the bright yellow, two determinations of the vapor density of mercury were made by the authors. Mercury was chosen for the reason, that inasmuch as its vapor consists already at a comparatively low temperature, of isolated atoms, the possibility of a further dissociation was avoided.

Two determinations were made, one at about 440° C., the other at 1567° C.

	Substance S.	Temperature t.	Barometer B.	Nitrogen volume V.
440° C.	0.0905 gm	20°.0 C.	722.3 mm	11.8 cc
1567° C.	0.0923 "	20°.5 C.	719.8 "	12.2 "

* The apparatus filled with nitrogen gas to prevent oxidation.

From these data they calculate the vapor density found at 440° C., 6.86 ; at 1567° C., 6.81 ; calculated for Hg., 6.91.

Further experiments to determine the dissociation of so-called elements were then commenced, and for these the following temperatures were selected : 620° C., 808° C., 1028° C., 1242° C., 1392° C. and 1567° C., which were carefully determined by means of a calorimeter.

In order to determine the density of oxygen gas at high temperatures, it was weighed as oxide of silver, in which the amount of silver had been carefully determined. This method of proceeding is, it may here be mentioned, the only one which may be applied, since the substance, the density of which is to be determined, must be weighed off and transferred into the apparatus in the manner described. The solid substance must be so selected that it will decompose quantitatively under the influence of the heat, into a solid residue and such substance as is wanted for the experiment.

In this case, oxide of silver was chosen, after it had been found that metallic silver is, at 1567° C., not volatile in any appreciable quantity. Two determinations of the silver oxide used, gave the following results :

		Ag. per cent.	
Substance taken.	Ag. found.	Found.	Calculated.
0.6688	0.6233	93.19	93.10
0.6037	0.5630	93.25	93.10

The density determinations of oxygen gave the following results, at 1392° C.

				DENSITY.	
Substance S (Ag_2O).	B	t	V	Found.	Calculated.
					O_2
0.2052 gm	719.3 mm	20° C.	12.00 cc	1.04	1.105
0.2095 "	719.3 "	20° C.	12.50 "	1.10	1.105

and at 1567° C.

0.2107 gm	719.3 mm	20° C.	12.50 cc	1.04	1.105
0.2174 "	719.3 "	20° C.	12.33 "	1.10	1.105

The molecules of the elements oxygen, nitrogen and sulphur, possess, therefore, at 1567° C., the same formulas which ordinarily are ascribed to them, O_2, N_2, S_2.

Entirely different results were obtained in the examination of chlorine.

Density of chlorine at high temperatures.—In order to weigh the chlorine, a substance had to be selected, which, on the application of heat, would easily and completely evolve it, and which, at the same time, would leave an absolutely non-volatile residue. As such substance, platinous chloride, Pt_2Cl_4, was selected. It is the more adapted

for such a purpose, as it is by no means hygroscopic, and can easily be obtained chemically pure.

Analyses made of this substance, which was obtained as an olive-green, very dry, powder, gave for Pt, 73.61, 73.39, 73.42—calculated, 73.54 ; for Cl, 26.35, 26.15—calculated, 26.64.

The following tabulated statement gives the results obtained in testing the density of chlorine at various temperatures.

Temperature.	$S(Pt_2Cl_4)$	B	t	V	DENSITY. Found.	DENSITY. Calculated. Cl_2
620°C.	0.1312 gm	722.3 mm	21°.0 C.	12.9 cc	2.42	2.45
"	0.1332 "	722.3 "	21°.0 C.	12.9 "	2.46	2.45
808°C.	0.1277 "	719.8 "	22°.5 C.	13.9 "	2.21	2.45
"	0.1335 "	719.8 "	22°.5 C.	14.7 "	2.19	2.45
1028°C.	0.0977 "	717.8 "	24°.0 C.	12.8 "	1.85	2.45
"	0.1056 "	717.8 "	24°.0 C.	13.6 "	1.89	2.45
1242°C.	0.0974 "	717.8 "	24°.0 C.	14.3 "	1.65	$\frac{2}{3}Cl_2$ 1.63
"	0.0997 "	717.8 "	23°.0 C.	14.5 "	1.66	1.63
1392°C.	0.0953 "	722.8 "	20°.5 C.	13.6 "	1.66	1.63
"	0.0956 "	717.8 "	23°.0 C.	13.8 "	1.67	1.63
1567°C.	0.0967 "	721.3 "	21°.5 C.	14.4 "	1.60	1.63
"	0.0973 "	721.3 "	21°.5 C.	14.4 "	1.62	1.63

From the above it is easily seen, that at about 800°C. a dissociation of the chlorine commences and gradually increases, until at 1242° C. it has become complete, the resulting substance having a density of $\frac{2}{3}$ of the density which belongs to chlorine at lower temperatures.

The molecular weight of chlorine, which to 600° C. is 71, is, therefore, above 1200° C., only 47.3.

To meet the objection that these results were obtained by the action of the chlorine upon the vessels composing the apparatus, the authors have made a number of experiments, which prove that this could not have been the case.