A SIMPLE METHOD OF DETERMINING VAPOR-DENSITIES¹

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Part I

Apparatus

The apparatus is of glass and consists of a stout, long bulb, having a tight-fitting stopper at one end, and at the opposite end, a long capillary-tube with a tap at its extremity. By means of a split cork, it can be fixed in a flask fitted with a condenser. The volume of the bulb (*i. e.*, when the stopper is in position) is determined once for all, and the capillary-tube has marked along it, a linear scale (cms divided into mm). Two threads of mercury are introduced, one to close the tap, the other near the bulb; the air-space between the two threads will serve as an air-manometer (a pressure-gauge). A weighed quantity of the substance to be experimented on is introduced in a small stoppered tube, a little mercury (1 cc) poured in, the stopper fixed and bound firmly to the neck with wire, the whole fixed in the flask, and then heated in the vapor of some liquid, boiling above the temperature at which the substance vaporizes. It will be observed that solid substances, as well as liquids, capable of existing in the state of vapor, can be dealt with

Fig. 1

¹ Read before a meeting of the Chemical Society, London, January 16th, 1908. Compare Chemical News, 97, 102 (1908).

by this method. The final reading is taken when the air in the gauge remains constant in volume. When the apparatus has cooled down, it may be heated to some other suitable temperature and a fresh reading taken; this process may be repeated any number of times, each giving an independent result.

Theory

Let p = the atmospheric pressure (mm) and t_1° = the temperature of the air, when the substance, of weight w , was introduced;

V = the volume of the bulb;

L, l = the lengths of the air-gauge at t_1° , and t_2° respectively;

Hh , = the respective volumes of the space in the capillary between the bulb and the movable mercury thread, at t_1° and t_2° ;

t_3° = the temperature of the heating vapor.

If a = the area of the cross section of the bore of the capillary-tubing, we have

$$(1) \text{ the final total pressure} = \frac{pLa(273 + t_2)}{la(273 + t_1)};$$

$$(2) \text{ the pressure of the air in the bulb} \\ = P(V + H)(273 + t_2)/(V + h)(273 + t_1);$$

$$(3) \text{ the pressure of the vapor, therefore,} \\ = (1) - (2) = \pi = \frac{p(273 + t_2)}{(273 + t_1)} \left(\frac{L}{l} - \frac{V + H}{V + h} \right).$$

The volume of the vapor at 0° and 760 mm = $273 \pi (V + h)/760(273 + t_2)$, and its density is = w divided by this last expression =

$$\frac{760 w(273 + t_1)}{273 p(V + h) \left(\frac{L}{l} - \frac{V + H}{V + h} \right)}.$$

When compared with the vapor-density of hydrogen at 0° and 760 mm (assuming that 1 gram of hydrogen occupies 11160 cc) the formula becomes

$$\frac{31068 w(273 + t_1)}{p(V + h) \left(\frac{L}{l} - \frac{V + H}{V + h} \right)}.$$

For ordinary purposes, however, seeing that h and H are generally very small compared with V , sufficiently accurate results, will be obtained by neglecting h and H and using the formula

$$\frac{31068 \, w l (273 + t_1)}{p V (L - l)}.$$

Indeed, the author found in practice that the results as calculated by means of this formula are scarcely 0.5 percent greater than if calculated by the preceding more complicated formula.

Precautions

(1) If water be used as the heating liquid, no condenser is required.

(2) It is most difficult to keep the stopper perfectly air-tight during an experiment. A small quantity (1 cc should be found quite sufficient) of mercury—allowance for its volume must be made in the calculations—is introduced into the bulb before the substance is introduced. The mercury will settle over the stopper and close effectively any space between it and the neck.

(3) When the gaseous pressure within the bulb is considerable, the mercury thread may be forced out round the tap. To avoid this occurring, the tap should be fastened firmly with wire to the capillary.

(4) In very accurate work, allowance will have to be made for the volumes of the tube and the contained substance.

(5) Generally, when a substance of unknown molecular weight is experimented on, not more than 0.1 gram of it, per 50 cc of bulb should be employed.

(6) No substance should be experimented on which is likely to affect the mercury.

(7) The thread of mercury closing the tap must be long enough to reach below the level of the outlet for the heating vapor. This will necessitate a fairly long thread, and allowance for its expansion, if it be considerable, may be made thus:

when the mercury has ceased to expand, the tap is very cautiously opened; the internal pressure will force the mercury outwards, and when the end of the thread has reached its initial position, the tap is turned off, after which the reading for l is taken.

(8) The other thread need not be much more than 1.0 cm in length and no allowance for its expansion will then be needed.

(9) If the apparatus be totally suspended from the cork within the vessel, both mercury threads may then be short and no allowance for expansion will then have to be made; however, there is some risk of the tap breaking when the apparatus is being heated.

(10) Before use, the apparatus should be thoroughly cleaned and dried, and a current of air drawn through it to remove any vapors.

(11) After the substance has been introduced into the bulb, the stopper must be immediately fixed and bound firmly with thin wire to the neck to prevent its moving while it is being fastened on, aided by pliers, with soft copper wire ($1/16$ to $1/20$ inch in diameter) to the neck. Care must be taken to wind the wire in the same direction, else it will be untwisted in one place while it is being tightened in another. During this operation, the apparatus should be held bulb downwards.

(12) The length of the air-thread in the manometer will be slightly lengthened, due to the weight of the movable mercury thread. The correct length l_c required is given by $\frac{L}{l} = \frac{L}{l_c} - \frac{M(273 + t_1)}{p(273 + t_2)}$ in which M is the length (mm) of the movable mercury thread.

(13) Clean, dry mercury only should be used.

Advantages

The apparatus is simple in construction and is, therefore, cheap and easily manipulated, and is capable of giving good results in a short time (30-45 minutes).

Results

The heating liquid employed was, in all the experiments, water, and no condenser was used. No determination failed to give a good result, when the stopper was well closed (as indicated by no expulsion of mercury). Allowance in every case was made for the volume of the weighing tube and the contained substance.

Substance	<i>w</i> gram	<i>l_c</i> mm	<i>t₁</i> ^o	<i>p</i> mm	V cc	<i>L - l_c</i> mm	Vapor density	
							Found	Theory
C ₂ H ₅ Br	0.073	85	10.5	750	27.3	48	55.25	54.48
"	0.279	36	15.5	750	26.0	88	52.26	54.48
C ₂ H ₅ I	0.159	59	14.5	747	29.3	54	70.64	77.92
" (purer)	0.157	63	16.5	750	29.2	55	72.54	77.92
CH ₃ .CO ₂ C ₂ H ₅	0.054	86	14.0	747	29.3	41	45.97	44.00
CH ₃ .CO.CH ₃	0.070	52	17.0	741	29.2	55	27.45	29.00
"	0.063	71	16.5	740	29.2	64	28.68	29.00
"	0.060	52	16.5	741	29.2	49	26.22	29.00
CH ₃ .CN	0.016	100	15.5	743	29.2	31	20.96	20.52
"	0.020	90	14.0	743	29.2	33	22.25	20.52
CH ₃ I	0.126	73	16.0	749	29.2	52	72.15	70.93
"	0.111	80	17.0	750	29.2	52	72.60	70.93
C ₆ H ₆	0.009	114	17.0	750	29.2	11	37.99	39.00
"	0.036	90	17.0	750	29.2	36	36.88	39.00
"	0.017	99	17.0	746	29.2	18	38.42	39.00
CH ₃ .OH	0.014	85	16.0	750	29.2	30	16.14	16.00
"	0.020	80	16.0	750	29.2	40	16.29	16.00
(C ₂ H ₅) ₂ O	0.018	105	17.0	748	29.2	20	38.75	37.00
"	0.020	105	16.5	748	29.2	22	39.09	37.00
"	0.014	105	15.5	750	29.4	16	37.07	37.00
C ₂ H ₅ .OH	0.018	86	16.5	750	29.4	26	24.07	23.00
"	0.021	90	17.0	750	29.2	33	23.39	23.00
CS ₂	0.021	104	16.0	745	29.2	23	38.81	38.06
"	0.030	97	17.0	746	29.2	30	39.82	38.06
"	0.061	80	16.5	746	29.2	50	40.00	38.06
CHCl ₃	0.021	112	15.5	759	29.2	16	58.66	59.67
"	0.024	111	15.5	759	29.2	18	59.13	59.67
CCl ₄	0.023	112	16.0	759	29.3	13	78.71	76.90
"	0.024	115	16.0	759	29.2	14	78.49	76.90

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Part II¹

Apparatus

The following modified form of the apparatus is one of the best means for determining vapor-densities, considering its simplicity, and the ease and accuracy with which results can be obtained. Its advantages over the first form of the apparatus are that (1) it contains neither tap nor joints, (2) it has no stopper; (3) a split cork for fixing is not required; (4) no mercury is necessary for sealing and (5) increased accuracy is obtained due to increase in V , L and l , and (if desired) w . The apparatus consists of two parts, a capillary-tube and a bulb.

Fig. 2

The capillary-tube may be either straight or U-shaped; in the latter case, greater values for L , L_c , and l are obtained. One end is sealed, and a scale of cms (divided into mm) is marked along it. A short thread of mercury is introduced into the open end, and the air-space of length L thus enclosed, serves as the air-manometer.

The bulb consists of a clean, dry, glass tube, sealed at one end; through the open end, the small stoppered weighing tube with its contained weighed quantity of the substance to be experimented upon is dropped in, the manometer is put in and the open end of the tube is sealed up. When the glass has again cooled down to t_1° , the length L_c of the air-thread in the manometer is observed (see Precaution (7) further on). The bulb is now suspended from the cork within a flask, or better, within

¹ Compare *Zeit. phys. Chem.*, 63, 48, 381 (1908).

a Victor-Meyer's-heating-jacket, and heated in the vapor of some suitable liquid.

When the reading for l has been made, the bulb is removed and left to cool; a small portion of the glass at one end of the bulb is cut off; and (neither the manometer nor the weighing-tube is to be removed) the volume V of the bulb is determined by dropping in water from a burette.

Theory

The formula to be applied when calculating the vapor-density is either

$$\frac{31068 w_c L_c (273 + t_1)}{p L (V + h) \left(L_c - l_c \cdot \frac{V + H}{V + h} \right)},$$

or preferably (because less complicated and giving almost equally correct results)

$$\frac{31068 w_c L_c (273 + t_1)}{p L V (L_c - l_c)},$$

Precautions

(1) To introduce the mercury, the capillary-tube is warmed by passing over a Bunsen-flame, the open end placed in mercury, and a thread allowed to run in as the glass cools; L is measured when the manometer has cooled to the room-temperature, t_1° .

(2) To clean the capillary-tube, shake it sharply to eject the mercury; introduce a little, pure, suitable solvent and shake it out; finally dry the tube. If it becomes too dirty to be cleaned thus, the sealed end is cut off, the bore thoroughly cleaned and dried and one end again sealed. If the bore be not absolutely clean and dry, then any impurity in it will, when the apparatus is being heated, vaporize and will thus cause not only error in l but also the expulsion of the mercury from the bore. The mercury also must be quite pure, otherwise, on the application of heat, it will break up into a number of drops and be expelled from the bore.

(3) The temperature, t_2° , of the heating medium should be considerably higher than that of the substance experimented on, as the latter (until completely vaporized) has to vaporize under continually increasing pressure.

(4) To suspend the bulb, some wire or string is wound round it, the ends being passed round the cork.

(5) The manometer can be placed with either (a) the open end, or (b) the closed end, towards the top. It should be possible to read L , L_c , and l accurately to half a mm.

(6) Allowance must be made for, (a) the compression, or (b) the extension (see (a) and (b) of Precaution (5)) of the air in the manometer due to the weight of the mercury-thread [(1) the pressure with the manometer horizontal = $\frac{pL(273 + t_2)}{l_c(273 + t_1)}$; (2) the pressure with the manometer vertical = $\frac{pL(273 + t_2)}{l(273 + t_1)}$; and, if M is the length measured in mm of the mercury-thread, (1) $\pm M = (2)$], the correct length l_c is given by the equation

$$\frac{1}{l} = \frac{1}{l_c} \pm \frac{M(273 + t_1)}{pL(273 + t_2)};$$

[+ in case (a), — in case (b)]. The correction is especially necessary when L_c and l do not differ greatly in the value, as the error for l_c in such cases may amount to as much as $\pm 3L_c/100$. The readings for L and L_c are taken with the manometer held horizontally and no such correction is needed.

(7) After the tube has been sealed and left to cool to t_1° , the internal pressure has changed (it always becomes less than p). The change in the internal pressure must be allowed for by observing the alteration that has been produced in L ; thus, if L (before sealing the bulb) changes to L_c (after the bulb has been sealed) the pressure alters to pL/L_c , and the formula must be written (by putting pL/L_c for p and L_c for L)

$$\frac{31068 wl_c L_c (273 + t_1)}{pL(V + h) \left(L_c - l_c \frac{V + H}{V + h} \right)}.$$

(8) When working with an extremely volatile substance, it is perhaps better to seal it up in a very thin glass tube (whose weight is known and subtracted from the combined weight of the substance and tube); this can be very easily broken (after the bulb has been sealed and L_c measured) by shaking the bulb to cause the manometer to strike against it, thus liberating the contained substance. This method of weighing should certainly be used when experiments are carried out upon very unstable substances.

Results

The heating medium was steam ($t_2 = 100^\circ$), and a condenser was not employed.

Substance	w gram	l_c mm	t_1 $^\circ\text{C}$	p mm	V cc	L mm	L_c mm	Vapor-density	
								Found	Theory
CH_3I	0.7562	156	16.5	759	94.9	363.5	364	70.78	70.93
$\text{C}_2\text{H}_5\text{I}$	0.2120	236	17.5	755	78.2	341	343	71.73	77.92
$\text{C}_2\text{H}_5\text{Br}$	0.3721	143	16.5	763	70.5	317	318	51.31	54.48
$\text{CH}_3\cdot\text{OH}$	0.1639	162	16.0	761	116.7	324.5	326.5	15.73	16.00
$\text{C}_2\text{H}_5\cdot\text{OH}$	0.1814	193.5	16.5	757	88.5	388.5	390	23.89	23.00
$(\text{C}_2\text{H}_5)_2\text{O}$	0.2810	155	16.0	756	88.2	314.5	316	36.52	37.00
$\text{CH}_3\cdot\text{CO}\cdot\text{OC}_2\text{H}_5$	0.1351	257.5	15.0	754	73.2	379	380.5	45.73	44.00
$(\text{CH}_3)_2\text{CO}$	0.1978	177	17.0	749	91.8	334	337.5	28.60	29.00
$\text{CH}_3\cdot\text{CN}$	0.2013	160	16.5	761	102.3	324.5	325.5	22.42	20.52
CS_2	0.4265	146	16.5	765	99.5	321.5	322.5	41.63	38.08
CCl_4	0.2448	232	16.0	765	68.4	363.5	365	75.15	76.90
CHCl_3	0.2176	271.5	16.5	766	90.2	393.5	395	62.01	59.67
C_6H_6	0.3230	166	17.0	755	97.5	336	337	38.35	39.00

Part III¹

If every precaution be taken to determine the various quantities correctly, and making all allowances in the calculations—see Precautions (6) and (7) in Part II—the method may be used for determining quickly and accurately, the constituents by weight of a mixture of two substances, or to determine the quantity of an impurity in a substance.

¹ Compare Zeit. phys. Chem., 63, 52 (1908).

and $w_1 + w_2 = w$, whence w_1, w_2 can be solved.

TABLE—(Continued)

Mixture	p mm	L mm	V cc	L_c mm	l_c mm	w grams	t_1 °C	Percent- ages
CH ₃ .OH	764	291	81.7	293	110	0.2164	16.5	50.0
C ₂ H ₅ .OH								50.0
CH ₃ .OH	764	300	77.6	303	111	0.1959	18.0	72.8
C ₂ H ₅ .OH								27.2
C ₂ H ₅ .OH	761	289	72.9	291	108	0.2889	15.0	18.1
CH ₃ .CO.CH ₃								81.9
C ₂ H ₅ .OH	761	311	68.2	315	119	0.2306	16.5	69.0
(CH ₃) ₂ CO								31.0
CH ₃ .CO.CH ₃	758	281	93.8	284	153	0.3024	15.0	43.1
CCl ₄								56.9
CO(CH ₃) ₂	758	282	90.0	286	145	0.2781	17.0	61.0
CCl ₄								39.0
C ₆ H ₆	760	265	85.5	270	121	0.2804	16.5	37.8
(CH ₃) ₂ CO								62.2
CCl ₄	761	279	81.4	282	132	0.3138	17.5	8.3
C ₆ H ₆								91.7

Part IV¹

The formula for calculating vapor-densities is independent of t_2 , the temperature to which the bulb is heated; therefore, once the substance experimented on is completely vaporized, any variations in the temperature as a whole will produce no change in l (l being the only quantity which can thus be appreciably affected), assuming that the molecular constitution of the substance does not suffer alteration during such variations in temperature; hence there is no necessity

¹ Compare Zeit. phys. Chem., 63, 635 (1908).

to use a heating medium boiling at constant temperature. This consideration points to a simple method for heating; the sealed bulb is placed in a wider piece of combustion tubing; a thermometer reading to 358° is put into another piece of tubing, to act as a safeguard against raising the temperature above 358° ; the two are then placed horizontally side by side and heated by means of an ordinary combustion furnace, or better in a trough containing some substance (*e. g.*, glycerine) which can be heated to a high temperature.

No allowance is necessary for the vapor-tension of the mercury-thread, for the tension within the manometer is equalized by that in the bulb; further, the pressure within the bulb is so considerable (it may rise to as much as 5 atmospheres or even more—consequently the need for surrounding the bulb with the thick combustion tubing to guard against possible risk of bursting, although the author himself has not in a single instance met with such an accident, though he carried out over fifty determinations at fairly high temperatures, many of them well above 300°) that the bulb may be heated above 358° , the boiling point of the mercury under normal pressures.

Seeing that the bulb is heated in a horizontal position, no correction is required for l , the formula to be used in calculation being either

$$\frac{31068 w l L_c (273 + t_1)}{\rho L (V + h) \left(L_c - l \frac{V + H}{V + h} \right)},$$

or preferably (because simpler and almost inappreciably less accurate)

$$\frac{31068 w l L_c (273 + t_1)}{\rho L V (L_c - l)}.$$

There is no need, whatever, to graduate the capillary-tube, for it is a very simple matter to read L correctly by means of a mm scale, and L_c and l by the aid of a pair of calipers or compasses or dividers, the distance between

the legs being then measured off along a mm rule or scale. (On account of the great heat, it is impossible to keep the eyes sufficiently near the bulb to observe the graduations if the manometer be graduated.) As the manometer consists simply of an almost inexpensive plain piece of capillary-tubing, it is most advisable to cut off the sealed end, thoroughly clean and dry the bore, and again seal one end every time before an experiment is performed.

From the results of experiments carried out (see the remarks further on) it is conclusively demonstrated that the method may, with safety, be used for determining the vapor-densities of substances which under ordinary conditions react chemically with mercury.

Not too long a thread of mercury should be introduced into the capillary, so that a good length of air-thread (*i. e.*, H) may be left between the open end of the manometer and the mercury-thread, for after sealing the bulb, L_c (Fig. 3) is invariably greater than L , and therefore, if no such provision (*viz.*, a fairly large value for H , from 2 to 3 cm) be made, some of the mercury from the thread may be expelled from the bore and fall into the bulb, thus spoiling the result of an experiment if the substance experimented on is capable of reacting upon mercury; otherwise (*i. e.*, when no such chemical reaction between the substance and mercury can take place) this overflow is of no importance, provided the mercury-thread is not entirely expelled from the bore.

Fig. 3

It is, by far, more preferable to use a trough containing some liquid, that may be raised to and maintained at some convenient temperature than a combustion furnace as the heating medium; for, with the latter it is not a very easy matter to ensure that both the bulb and the manometer (which, in considering this question, it must not be forgotten, consists of a thick-walled capillary-tube) are at pre-

cisely the same temperature; of course, if the heating method as explained in Part II—(rather difficult of manipulation and calculation comparatively)—be used, this temperature difficulty entirely disappears, though, then the range of heating temperatures (t_2°), *i. e.*, the number of suitable heating liquids, as compared with a thermostatic method is rather limited. The thermostatic method is undoubtedly the best.

Results

The author employed in all cases a combustion furnace. The temperature was generally raised to about 50° above the temperature at which each respective substance vaporizes under ordinary atmospheric pressures; the flames were then turned out and the tubes covered with asbestos and left for about five minutes to allow both bulb and manometer to assume throughout as uniform a temperature as possible, after which l was measured in the manner indicated above. It will be observed that the substances experimented on are fairly representative, including organic and inorganic bodies, both solid and liquid substances.

Iodine gives such an extremely dark vapor that it was repeatedly found impossible to see the mercury-thread when the bulb was heated to the required temperature (t_2°). This difficulty was overcome by the following device. The manometer was pressed close to the bulb, prior to sealing, by resting it on two pieces of glass rod of suitable thickness; the bulb was then placed so that the manometer was to the top, and on heating it was found quite easy to observe both manometer and mercury-thread. All substances which give dark-colored vapors on heating, should be dealt with in this manner.

*Apparently no appreciable interaction took place between the mercury and these substances, probably owing to the small exposed surface presented by the outward end of the mercury-thread, and very likely also due to the prevention of diffusion of the vapors of these substances within the narrow bore of the capillary-tube and the interposition of

Substance	w gram	l mm	t ₁ °C	p mm	V cc	L mm	L _c mm	Vapor-density	
								Found	Theory
C ₅ H ₅ N	0.0836	155	16.5	760	38.4	254	258	39.25	39.50
C ₈ H ₁₁ .OH	0.0763	165	15.5	763	30.0	268	277	44.16	44.00
C ₈ H ₅ .OH	0.0621	138	17.0	762	29.0	266	278	25.87	29.00
(CH ₃ .CO) ₂ O	0.1594	147	16.5	763	30.8	316	321	52.35	51.00
CH ₃ .COCl	0.1231	135	16.0	765	45.1	238	255	39.51	39.22
CH ₃ .COH	0.0340	128	15.0	756	36.6	190	192	22.22	22.00
H ₂ O	0.0346	161	16.0	753	44.3	326	329	9.01	9.00
C ₂ H ₄ Cl ₂	0.1641	163	16.0	756	38.9	323	329	49.99	49.45
C ₂ H ₄ Br ₂	0.0885	204	16.5	756	44.2	251	256	95.38	93.96
CH ₃ .CO ₂ H	0.0659	176	17.0	750	30.1	330	337	29.36	30.00
C ₆ H ₅ .NH ₂	0.1208	193	16.5	761	29.5	380	390	48.66	46.52
C ₂ O ₂ (O.CH ₃) ₂	0.1722	177	16.5	761	40.0	326	340	58.83	59.00
C ₆ H ₅ .NO ₂	0.1020	108	15.0	768	22.1	190	201	65.99	61.52
CHBr ₃	0.1599	193	16.5	765	24.9	299	310	128.89	126.44
* POCl ₃	0.1495	145	17.5	753	26.9	267	277	75.91	76.67
* PCl ₃	0.1466	134	16.0	755	24.0	273	288	66.69	68.67
* S PCl ₅	0.0727	163	17.5	760	22.6	271	285	51.63	104.12
* I	0.0879	160	23.5	760	22.1	205	230	123.6	126.8
* Br	0.1239	137	15.5	767	22.4	242	260	77.35	79.96
S CH ₃ .CH(OH).NH ₂	0.0355	167	18.0	760	38.6	283	294	14.94	30.52
C ₆ H ₄ (OH).COH	0.1390	174	19.5	760	34.1	325	334	54.47	61.00
C ₆ H ₅ .COH	0.1499	156	19.5	760	32.3	310	320	54.48	53.00
CHCl ₂ .CO ₂ H	0.1341	126	19.0	761	29.5	220	234	67.24	64.45
CH ₃ .CO.NH ₂	0.1180	99	19.0	761	25.2	269	279	31.85	29.52
C ₆ H ₅ .NH.CH ₃	0.1068	140	18.0	763	20.5	306	318	50.46	53.52
C ₆ H ₅ .N(CH ₃) ₂	0.1148	139	18.5	763	26.6	245	256	61.44	60.52
<i>o</i> -CH ₃ .C ₆ H ₄ .NH ₂	0.1378	144	17.0	762	24.5	319	328	53.51	53.52
<i>p</i> -CH ₃ .C ₆ H ₄ .NH ₂	0.1392	145	17.5	762	22.7	340	350	52.89	53.52
(C ₆ H ₅) ₂ NH	0.1606	147	17.0	764	39.0	224	236	84.50	84.52
C ₆ H ₅ .NH.CO.CH ₃	0.1700	129	18.0	766	36.1	232	241	66.50	67.52
S CCl ₃ .CH(OH) ₂	0.0895	143	16.5	765	29.4	229	240	55.29	82.67
C ₆ H ₅ .COCl	0.1542	165	16.0	763	26.8	326	335	67.53	70.22
C ₆ H ₅ .CH ₂ Cl	0.1479	141	17.0	763	24.5	296	306	62.97	63.22
<i>p</i> -NH ₂ .C ₆ H ₄ .Cl	0.1337	158	17.5	763	23.1	321	332	64.29	63.74
<i>p</i> -CH ₃ .C ₆ H ₄ .NO ₂	0.1405	120	17.0	761	38.9	192	201	66.32	68.52
β-C ₁₀ H ₇ .OH	0.1296	117	18.0	765	34.2	180	194	73.34	72.00
α-C ₁₀ H ₇ .NH ₂	0.1300	133	19.0	762	29.5	220	232	74.32	71.52

the long narrow cylindrical layer of air therein. Indeed, the fact that in these cases the vapor densities determined are not greater than the theoretical ones proves that no action between the mercury and these substances had taken

place; for, had it been otherwise, it is quite evident that the loss of any of the substance in any particular case would have resulted in a lower pressure of vapor in the bulb with a consequent greater value for l , and therefore also a smaller value for $L_c - l$, than those theoretically required, both these quantities tending to make the calculated result greater than the theoretical one.

§ Evidently the PCl_5 dissociated into PCl_3 and Cl_2 , and the $\text{CH}_3\text{CH}(\text{OH})\text{NH}_2$ into CH_3CHO and NH_3 ; in the case of the chloralhydrate about 57.6 percent of it decomposed into CCl_3CHO and H.OH at the temperature of about 150° .

It will be found much more advantageous to use the method here given than that in Part III., as not only is it simpler and easier to calculate by its aid on account of its consisting of only one equation, but also it gives directly the percentage composition, whereas by the former method the percentage composition can only be obtained by further calculation.

Let w_1 be the percentage weight required of one of the constituents (of vapor-density d_1 , supposed to be known), then $100 - w_1$ is that of the other component (of vapor-density d_2 , also assumed known), and $w_1 + 100 - w_1$ or 100 is the total weight of the mixture. Now at 0° and 760 mm pressure

(1) the volume of the first component = $11160 w_1 \div d_1$;

(2) the volume of the second constituent = $11160(100 - w_1) \div d_2$;

(3) the volume of the mixture = $11160 \times 100 \div$ the vapor density of the mixture

$$= \frac{11160 \times 100 p L V (L_c - l)}{31068 w L_c (273 + t_1)};$$

but, (1) + (2) = (3); hence, on simplifying the resulting expression we obtain the equation

$$d_2 w_1 + d_1 (100 - w_1) = \frac{100 d_1 d_2 p L V (L_c - l)}{31068 w L_c (273 + t_1)},$$

from which w_1 , and $100 - w_1$, can be solved.

Mixture	p mm	L mm	V cc	L_c mm	l mm	w gram	t_1 °C	Percent- ages
$C_6H_5 \cdot CO \cdot NH_2$	760	301	45.3	310	200	0.1504	18.0	45.84
$C_6H_5 \cdot N : N \cdot C_6H_5$								54.16
$m\text{-}C_6H_4(OH)_2$	760	295	42.5	306	191	0.1487	18.0	27.85
$C_{10}H_7 \cdot Cl$								72.15
$p\text{-}CH_3 \cdot C_6H_4 \cdot OH$	765	293	40.9	301	187	0.1410	17.5	15.15
$\alpha\text{-}C_{10}H_7 \cdot OH$								84.85
$\beta\text{-}C_{10}H_7 \cdot NH_2$	765	280	38.7	294	193	0.1572	18.0	34.60
$p\text{-}C_6H_4Br_2$								65.40
$m\text{-}HO \cdot C_6H_4 \cdot CH_3$	763	295	36.1	308	188	0.1225	16.0	35.89
$C_6H_4(CO)_2O$								64.11
$C_{10}H_8$	763	210	33.8	220	128	0.1273	16.5	86.17
$o\text{-}NO_2 \cdot C_6H_4 \cdot OH$								13.83

The apparatus, and the equation above given, may be used in the study of the dissociation of decomposable compounds.

Part V¹

The following apparatus will obviate the necessity for measuring V and for sealing the apparatus, though the introduction of the stopper will prevent its use at high temperatures (above 200°) due to risk of cracking the neck.

The bulb has at one end a conical mouth, the narrower end to face outwards with a perfectly ground, air-tight stopper to fit. When making the apparatus, the other end is sealed up after the stopper has been put in. The stopper should have a long handle of the shape shown to permit its being drawn outwards to close the mouth. After the manometer

¹ Compare Zeit. phys. Chem., 63, 639 (1908).

and substance have been introduced the stopper is pulled into position; when heated the internal pressure of the contained air and vapor will fix the stopper tightly, the greater the internal pressure the closer the fit. To open the mouth again, the bulb is cooled, and the internal pressure diminished by cooling the bulb with a few drops of ether; on slightly

tapping the stopper, it will be forced inwards by the relatively greater external pressure; it is advisable to wind loosely a piece of string round the handle of the stopper and the neck of the bulb, otherwise the stopper as it flies inwards may strike the bulb with sufficient force to break it.

To test the air-tightness of the stopper, a little ether is poured into the bulb, the stopper fixed, and the whole immersed in warm water; if no bubbles of ether escape, the stopper fits properly.

The volume of the bulb is determined once for always. The stopper is fixed to prevent its moving, and the bulb placed in a vessel, mouth upwards; water is poured in to cover the stoppered bulb; the stopper is now allowed to fall down, and more water is added from a burette to fill the bulb and reach the same level as before; this extra volume of water represents the volume of the bulb. When working with it, allowance must of course be made for the volumes of the manometer and of the weighing-bottle.

The internal diameters of the neck and of the body of the bulb should be sufficiently large to allow the manometer to be inserted with ease and to get past the stopper without difficulty.

With this apparatus it will be found that L and L_c are equal (or generally very near so).

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Fig. 4