

A COMPARATIVE METHOD FOR DETERMINING VAPOR DENSITIES. II

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Expansion of the Mercury

It is interesting to note that $(V_1 + V_2) > (v_1 + v_2)$. When the apparatus is heated, the mercury must expand, and as the expansion of mercury is about seven times that of glass, the mercury can expand mainly only at the expense of the volumes of the gases in the bulbs; consequently the sum of the gas-volumes at t_2° is less than the sum of the air-volumes at t_1° . The coefficient of cubical expansion of mercury is 0.00018; if its volume at t_1° be M , then its volume at t_2° is $M(1 + 0.00018[t_2 - t_1])$, and the increase $= M(t_2 - t_3) 0.00018$; and so—not neglecting the comparatively insignificant expansion of the glass—

$$v_1 + v_2 + M(t_2 - t_1)0.00018 - (v_1 + v_2)(t_2 - t_3)0.000026 = V_1 + V_2.$$

This consideration, however, does not in any way affect or enter into either the practice or the theory of the method.

Expansion of the Glass-Bulbs

One may, with justice, assume that allowance should be made for the expansion of the bulbs; but, as is shown here, it may be entirely left out of account in practice.

Let the room-temperature when v_1 and v_2 are measured be t_3° (it will not differ considerably from t_1°).

The coefficient of linear expansion of glass is 0.0000086; therefore the coefficient of cubical expansion is $0.0000086 \times 3 = 0.000026$ nearly.

At t_2° , v_1 was $v_1 (+ [t_2 - t_3] 0.000026)$ and v_2 was $v_2(1 + [t_2 - t_3] 0.000026)$. Substituting these corrected values for v_1 and v_2 , respectively, in the formula, we have

$$\left\{ \frac{(p-m)\left(V - \frac{w_1}{s_1}\right)}{V - \frac{w_1}{s_1}} = m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\}$$

$$\left\{ \frac{V_1 - \frac{w_1}{s_1}}{v_1(1 + [t_2 - t_3]0.000026)} - \frac{V_2 - \frac{w_2}{s_2}}{v_2(1 + [t_2 - t_3]0.000026)} \right\}$$

$$= \frac{m_2}{273 + t_2} + \frac{31068 w_1}{d_1 v_1} = \frac{31068 w_2}{d_2 v_2}$$

or

$$\left\{ \frac{1}{1 + (t_2 - t_3)0.000026} \right\} \left\{ \frac{(p-m)\left(V - \frac{w_1}{s_1}\right)}{V_1 - \frac{w_1}{s_1}} = m_1 \right\}$$

$$\left\{ \frac{1}{273 + t_1} \right\} \left\{ \frac{V_1 - \frac{w_1}{s_1}}{v_1} - \frac{V_2 - \frac{w_2}{s_2}}{v_2} \right\}$$

$$= \frac{m_2}{273 + t_2} + \frac{31068 w_1}{d_1 v_1} = \frac{31068 w_2}{d_2 v_2}.$$

On making the actual calculations, the term

$$\frac{1}{1 + (t_2 - t_3)0.000026}$$

reduces the value of

$$\left\{ \frac{(p-m)\left(V - \frac{w_1}{s_1}\right)}{V_1 - \frac{w_1}{s_1}} = m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\} \left\{ \frac{V_1 - \frac{w_1}{s_1}}{v_1} - \frac{V_2 - \frac{w_2}{s_2}}{v_2} \right\}$$

by at most 0.01, thus producing a change of ± 0.01 in the value of $31068 w_1/d_1 v_1$, equivalent to less than $\pm 0.1\%$, which is insufficient to produce any alteration in the first decimal figure of d_2 .

In an experiment with diethyl ether, $(C_2H_5)_2O - d_1 = 37.0$, $s_1 = 0.73$ — and ethyl alcohol, $C_2H_5.OH - d_2 = 23.0$, $s_2 = 0.79 - p = 753$ mm, $t_1^\circ = 16$, $t_2 = 185^\circ$, $t_3 = 15^\circ$, $m = 3$ mm, $m_1 = 0$, $m_2 = -15$ mm, $V = 3.25$ cc, $V_1 = 3.55$ cc, $V_2 = 3.75$ cc, $v_1 = 3.00$ cc, $v_2 = 4.05$ cc, $w_1 = 0.0605$ gram, $w_2 = 0.0524$ gram, (A cooled), (M = 8.2) then assuming $d_1 = 37.0$, d_2 unknown, d_2 calculated = 22.986 and 22.983.

If in the equation

$$\left\{ \frac{(p-m)\left(V - \frac{w_1}{s_1}\right)}{V_1 - \frac{w_1}{s_1}} = m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\} \left\{ \frac{V_1 - w_1/s_1}{v_1} - \frac{V_2 - w_2/s_2}{v_2} \right\} \\ = \frac{m_2}{273 + t_2} + \frac{31068 w_1}{d_1 v_1} = \frac{31068 w_2}{d_2 v_2},$$

(I) w_2 is put equal to 0, the equation becomes

$$\left\{ \frac{(p-m)\left(V - \frac{w_1}{s_1}\right)}{V_1 - \frac{w_1}{s_1}} = m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\} \\ \left\{ \frac{V_2}{v_2} - \frac{V - \frac{w_1}{s_1}}{v_1} \right\} - \frac{m_2}{273 + t_2} = \frac{31068 w_1}{d_1 v_1}.$$

(NOTE. $+\frac{m_2}{273 + t_2}$ in the original equation, because as is seen under I further on, the mercury in B stands on a higher level than in A); and (II) w_2 is put equal to 0, the equation becomes

$$\left\{ \frac{(p-m)V}{V_1} = m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\} \\ \left\{ \frac{V_1}{v_1} - \frac{V_2 - \frac{w_2}{s_2}}{v_2} \right\} - \frac{m_2}{273 + t_2} = \frac{31068 w_2}{d_2 v_2}.$$

(NOTE. $-\frac{m_2}{273 + t_2}$ in the original equation, because as is seen under II further on, the mercury in B stands on a lower level than in A).

These two equations show that the apparatus may be used in two ways for determining the vapor density of a substance *directly* (that is, without having to employ a second substance for comparison) thus greatly simplifying the manipulation and reducing the chances of error.

The following are brief but clear descriptions of the simplified alternative methods.

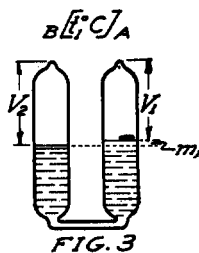
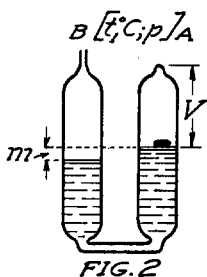
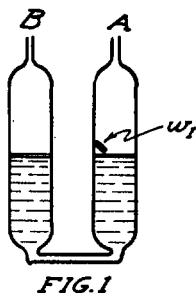
I and II

In both cases the apparatus consists of two bulbs (4 to 6 inches long), made of disused graduated tubing (*e. g.*, burette) joined together by a narrow U-tube (see Note 1 at the end). The bulbs are open at the free ends which are drawn off narrow. They are filled at least half full with pure dry mercury. The substance to be experimented on is introduced into a thin glass tube (see Note 2)—which has been previously weighed—and weighed, the difference giving the weight w_1 or w_2 (see I or II, respectively) of the enclosed substance (see Note 3).

I

The weighing tube is placed in one bulb A (Fig. 1), which is sealed, and when it has cooled to room-temperature t_1° the position of the mercury is noted, so that the volume V of the contained air can be afterwards determined. The difference in height m between the mercury levels is measured (see Note 4). The external atmospheric pressure p is observed, and the specific gravity s_1 of the substance is determined (Fig. 2).

The other bulb, B, is sealed, and when it has cooled to room-temperature, the positions of the mercury in A and B are noted in order to determine later the respective volumes V_1 and V_2 of the air enclosed. The difference in height m_1 between the mercury levels is measured (Fig. 3).



The apparatus is placed upright in a deep beaker containing a suitable heating medium, *e. g.*, glycerin or paraffin-

wax, and heated to t_2° to cause complete vaporization of the substance. The positions of the mercury in A and B are noted in order to measure later the respective volumes v_1 and v_2 of the enclosed gases and also to determine the difference in height m_2 between the mercury levels (Fig. 4).

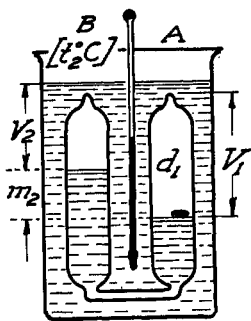


FIG. 4

The apparatus is removed, the room-temperature t_3° is noted; m_2 is measured; the bulbs are cut off, the mercury is removed, and mercury is poured into the bulbs from a burette to determine V , V_1 , V_2 , v_1 , and v_2 (see Note 5). All measurements throughout are carried out with the apparatus in a vertical position. The vapor density d_1 is then calculated from the formula

from the formula

$$\left\{ \frac{(p-m)\left(V - \frac{w_1}{s_1}\right)}{V_1 - \frac{w_1}{s_1}} \pm m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\} \left\{ \frac{V_2}{v_2} - \frac{V_1 - \frac{w_1}{s_1}}{v_1} \right\} - \frac{m_2}{273 + t_2} = \frac{31068 w_1 (1 + [t_2 - t_3] 0.000026)}{d_1 v_1} \dots \dots \dots (1)$$

or from the almost equally accurate but simpler formula

$$\left\{ \frac{(p-m)V}{V_1} \pm m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\} \left\{ \frac{V_2}{v_2} - \frac{V_1}{v_1} \right\} - \frac{m_2}{273 + t_2} = \frac{31068 w_1 (1 + [t_2 - t_3] 0.000026)}{d_1 v_1} \dots \dots \dots (2)$$

or (when no great degree of accuracy is required) from the formula

$$\left\{ \frac{(p-m)V}{(273 + t_1)V_1} \right\} \left\{ \frac{V_2}{v_2} - \frac{V_1}{v_1} \right\} = \frac{31068 w_1 (1 + [t_2 - t_3] 0.000026)}{d_1 v_1} \dots (3)$$

(for $\{1 + [t_2 - t_3] 0.000026\}$ see Note 6).

See Table I.

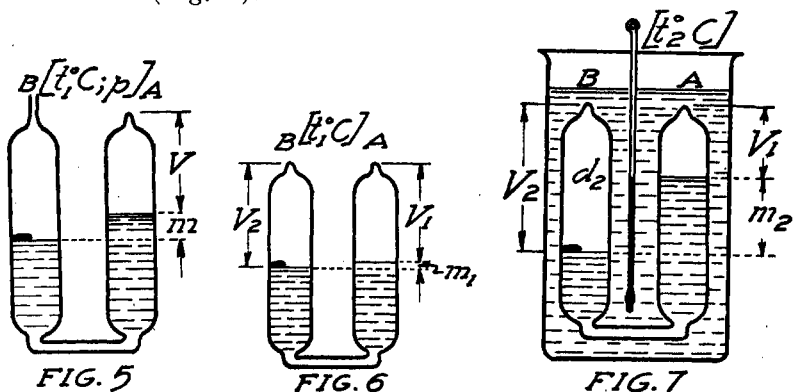
TABLE I

	ρ mm	α°	β°	δ°	m mm	m_1 mm	m_2 mm	V cc	V ₁ cc	V ₂ cc	v_1 cc	v_2 cc	w_1 gram	S ₁	d_1			
															(1)	(2)	(3)	Theory
Toluene	750	14	197	15	3	-2	46	4.25	4.55	4.70	6.50	2.50	0.0265	0.87	46.0	46.2	45.4	46.0
Pyridine	753	13	188	15	1	-4	47	3.95	4.15	4.10	6.00	2.00	0.0250	1.00	39.5	39.6	38.2	39.5
Methyl alcohol	756	15	120	16	3	4	45	4.15	4.35	4.00	6.10	2.05	0.0093	0.78	15.9	15.4	15.4	16.0
Ethyl alcohol	763	16	157	16	4	-3	51	3.60	3.80	5.85	7.45	2.00	0.0314	0.80	22.4	22.6	21.9	23.0
Methyl cyanide	765	18	127	19	2	2	57	4.05	4.35	5.00	7.05	2.10	0.0171	0.79	18.1	18.2	17.5	20.5
Ethylene chloride	764	17	171	18	4	2	23	3.05	3.15	4.20	5.20	1.95	0.0322	1.26	49.5	49.6	49.2	49.4
Ether (diethyl)	767	18	164	19	7	-15	47	3.15	3.45	5.45	6.10	2.50	0.0270	0.72	37.2	37.3	35.9	37.0
Carbon tetrachloride	766	14	188	16	6	3	62	5.65	5.95	5.95	8.25	3.35	0.0516	1.61	76.9	77.1	73.6	76.9
Acetone	766	19	173	19	8	1	39	4.80	4.95	5.00	7.05	2.65	0.0190	0.79	29.0	29.0	28.2	29.0
Chloroform	751	17	150	19	5	-1	43	4.55	4.85	4.65	6.50	2.45	0.0284	1.50	58.0	58.0	57.9	59.7
Acetaldehyde	752	14	155	16	2	3	43	4.00	4.20	4.35	6.00	2.45	0.0123	0.80	24.7	24.7	23.9	22.0
Amyl nitrite	754	16	181	18	3	-5	41	4.55	4.75	4.70	6.55	2.65	0.0301	0.87	57.0	57.1	54.9	58.5
Benzene	761	19	160	19	5	-3	40	4.30	4.40	4.60	6.20	2.55	0.0207	0.88	39.0	39.1	37.6	39.0
Amyl acetate	759	13	196	16	4	0	38	3.85	4.20	4.40	6.15	2.20	0.0368	0.88	60.0	60.1	58.7	65.0
Ethyl acetate	757	20	167	20	1	1	30	3.30	3.45	6.05	7.00	2.35	0.0544	0.90	47.0	47.1	46.5	44.0
Amyl alcohol	755	15	194	16	3	0	69	4.75	4.05	5.55	7.30	2.10	0.0649	0.81	44.1	45.0	43.4	44.0

II

One bulb, A, is sealed, allowed to cool to room-temperature t_1° and the position of the mercury in it is noted in order to determine later the volume V of the enclosed air. The difference in height m between the mercury levels is measured (Fig. 5).

The weighing tube is introduced into the other bulb, B, which is sealed and left to cool to room-temperature. The positions of the mercury in both bulbs A and B are noted so that the volumes V_1 and V_2 , respectively, of the enclosed air can be determined later. The difference in height m_1 between the mercury levels is measured. The atmospheric pressure P is observed, and the specific gravity s_2 of the substance determined (Fig. 6).



As described under I, the apparatus is heated to cause complete vaporization of the substance, and the quantities t_3 , V , V_1 , V_2 , v_1 , v_2 and m_2 are determined (Fig. 7). The vapor density, d_2 , is then calculated from the formula

$$\left\{ \frac{(p - m)V}{V_1} = m_1 \right\} \left\{ \frac{1}{273 + t_1} \right\} \left\{ \frac{V_1}{v_1} - \frac{V_2}{v_2} - \frac{w_2}{s_2} \right\} - \frac{m_2}{273 + t_2} \\ = \frac{31068 w_2 (1 + [t_2 - t_3] 0.000026)}{d_2 v_2} \dots \dots \dots (1)$$

or from the almost inappreciably less accurate formula

$$\left\{ \frac{(p-m)V}{V_1} = m_1 \right\} \left\{ \frac{1}{273+t_1} \right\} \left\{ \frac{V_1}{v_1} - \frac{V_2}{v_2} \right\} - \frac{m_2}{273+t_2}$$

$$= \frac{31068w_2(1 + [t_2 - t_3]0.000026)}{d_2v_2} \dots\dots\dots (2)$$

or (when great accuracy is not required) from the formula

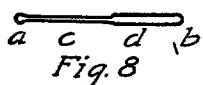
$$\left\{ \frac{(p-m)V}{(273+t_1)V_1} \right\} \left\{ \frac{V_1}{v_1} - \frac{V_2}{v_2} \right\} = \frac{31068w_2(1 + [t_2 - t_3]0.000026)}{d_2v_2} \dots\dots\dots (3)$$

See Table II.

The modified method and apparatus as described under I and II are analogous to the far simpler—and better in every respect—method and apparatus of the author's, described in the *Zeitschrift für Physikalische Chemie*, 65, 549-552 (1909), *Journal of Physical Chemistry*, 12, 671-677 (1908), and *Chemical News*, 100, 174 (1909). (See also *Journal of Physical Chemistry*, 15, 871 (1911), and *Chemical News*, 113, 241 (1916).)

Note 1 (upon the bulb).—The bulbs are joined by a narrow U-tube, instead of the whole being made of one wide tube bent into U-shape, to avoid using a greater quantity of mercury, the expansion of which must necessarily reduce even if only to a small extent the limited vaporizing capacity of the bulbs.

Note 2 (upon the weighing tube).—It is generally unnecessary to seal up the weighing tube. When experimenting with any volatile substance the weighing tube was made extremely thin, and dumb-bell shaped (Fig. 8; *a*, sealed, *b*, sealed; *d*, substance enclosed), the neck *c* being of hair-thinness and breaking immediately on agitating the mercury.



On several occasions a thin-walled tube, sealed, was enclosed with a short piece of glass rod to break it on agitation, in these cases V , V_1 , V_2 , v_1 and v_2 being corrected for the volume of this piece of glass rod, but this procedure is not at all desirable, because it reduces considerably the available vaporizing volume of the bulb.

The simplest and most effective weighing tube is the following: The substance is weighed out in a short, narrow, thin-walled glass tube closed at one end, the open end being

TABLE II

	ρ mm	t_1°	t_2°	t_3°	m mm	m_1 mm	m_2 mm	V cc	V_1 cc	V_2 cc	η_1 cc	η_2 cc	w_2 gram	s_2	d_4			
															(1)	(2)	(3)	Theory
Ethylene chloride	757	13	134	16	4	—4	53	5.65	5.85	5.20	3.00	7.85	0.0390	1.27	49.4	49.3	47.3	49.4
Amyl nitrite	764	14	181	16	3	—3	33	5.05	5.15	4.95	2.70	7.05	0.0423	0.87	57.0	56.9	55.5	58.5
Acetaldehyde	762	16	120	17	5	5	46	5.25	5.50	5.05	3.05	7.20	0.0154	0.80	25.0	24.9	24.2	22.0
Methyl cyanide	760	15	174	16	2	0	54	5.05	5.20	5.30	2.20	8.00	0.0195	0.79	18.1	18.1	18.6	20.5
Amyl alcohol	756	18	188	19	3	5	55	4.65	4.95	4.75	2.25	7.15	0.0368	0.80	44.0	44.1	43.0	44.0
Toluene	747	17	190	17	7	2	48	6.75	6.90	3.45	3.00	7.05	0.0478	0.87	46.0	46.0	46.7	46.0
Benzene	750	17	157	19	4	—5	49	5.50	5.80	5.05	3.20	7.40	0.0244	0.89	38.9	38.8	37.3	39.0
Carbon tetrachloride	758	18	163	18	8	2	51	4.80	5.00	5.05	2.50	7.20	0.0555	1.61	76.8	77.1	77.4	76.9
Acetone	763	20	149	20	5	—4	40	4.25	4.55	4.55	2.55	6.25	0.0143	0.79	29.0	28.9	27.9	29.0
Pyridine	768	16	191	16	4	0	47	3.90	4.00	5.05	2.00	6.85	0.0274	1.00	39.4	39.7	38.4	39.5
Ethyl ether	754	17	151	18	6	3	53	6.45	6.85	6.05	4.05	8.65	0.0236	0.72	37.0	37.1	35.8	37.0
Chloroform	755	16	155	17	5	25	43	5.85	6.00	4.25	3.00	7.00	0.0464	1.50	58.0	58.1	57.3	59.7
Ethyl alcohol	757	16	150	18	3	—2	48	4.95	5.25	5.75	3.30	7.45	0.0102	0.80	22.6	22.5	21.2	23.0
Methyl alcohol	759	15	180	17	6	—17	50	7.00	7.20	4.85	3.80	8.10	0.0124	0.78	15.9	15.7	14.0	16.0
Ethyl acetate	758	17	188	18	2*	0	59	5.50	5.85	5.50	3.15	8.00	0.0332	0.91	47.2	47.3	45.1	44.0
Amyl acetate	760	19	193	20	0	—1	55	3.90	4.00	6.25	2.00	8.00	0.0459	0.87	60.0	60.3	57.9	65.0

* See Note 4.

inserted in another similar, but slightly wider tube, the outer covering being included in the weighings and the tubes handled with a pair of clips and not with the bare fingers; this method proves quite effective in preventing loss of substance by evaporation. The liquid to be experimented on is introduced into the tube by the aid of simple glass re-fill made by drawing out fine one end of a piece of glass tubing.

If the substance be a non-volatile solid, it is simply weighed out in a very thin-walled glass tube.

In all cases the weighing tube is best made from thin test-tube glass, as it is then extremely thin-walled and of negligible volume.

Note 3 (upon w_1 and w_2).—As the available vaporizing volumes of the bulbs are small it is advisable to use only very small weights (w_1 , w_2) of substances, firstly, to facilitate rapid evaporation and, secondly, to avoid the gases in one bulb being of such a great volume as to force the mercury completely out of that bulb into the other (though this evidently must be impossible if the bulbs are originally more than half full of mercury).

Note 4 (upon m).—After one bulb has been sealed and left to cool to room-temperature, more mercury may be added to the other bulb until the mercury is on the same level in both bulbs, so that $m = 0$, after which the V-position is observed; but in actual practice there is as little trouble in measuring m and in making the necessary allowance in the calculation as in manipulating the mercury to make $m = 0$.

Note 5 (upon measuring V , V_1 , V_2 , v_1 , v_2).—The volume of mercury poured in to reach the volume—(V , V_1 , V_2 , v_1 , v_2) positions do not represent the *true* volumes occupied by the air or gases as the case might be, the true volume being more than this. The correction is easily made.

Suppose (Fig. 9) the mercury reaches a position which may be called the V-mark; then the true volume V is equal to the volume between this mark and the upper end, A, of the tube *plus* the volume, Z , of the triangular-shaped annular space between this mark and the mercury. Now, on invert-

ing the tube (Fig. 10) so that A is downward, the mercury is poured in to reach this V-mark; but the true total volume of the original air (or gas) was clearly as far as the upper curve corresponding to the mercury surface in Fig. 10, that is, it is short by an amount equal to $2Z$. Thus a volume equal to $2Z$ must be added in each case.

This quantity $2Z$ may be thus determined: The tube, or a piece of the original tube, open at both ends, has one end evenly closed with a flat stopper, and mercury, of volume A, is poured in from a burette up to any convenient height c (Fig. 11); the volume B of the mercury between the stopper a

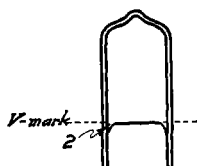


Fig. 9

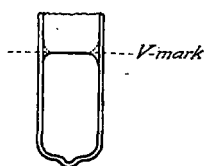


Fig. 10

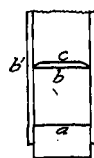


Fig. 11

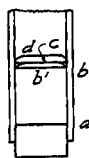


Fig. 12

and the point of contact b' of the mercury meniscus and the glass is read off by aid of the graduations on the tube; the tube is next viewed from one side so that the position b' is in front, (Fig. 12), and more mercury of volume c is added until the point of contact of the mercury meniscus and glass is now on a level with c . The volume between b' and $c = A - B =$ the volume between c and d ; but the total volume between bc and $d = C = (A - B) + 2$, whence $2Z = 2c - 2A + 2B =$ amount to be added.

Hackney Technical Institute
London