THE RELATIONSHIP OF THE HEAT OF VAPORIZATION OF GASES TO THEIR DENSITY AND ALSO TO THEIR BOILING-POINT.

BY WM. L. DUDLEY.

Received September 27, 1895.

IN studying the heat of vaporization or latent heat of various gases it soon became apparent that this constant bore an interesting relationship to their density and boiling-point. To trace out this relationship I have endeavored to obtain the latest and best latent heat determinations, as well as the specific gravity of the liquids at the boiling-point. Accurate data of this kind are scarce, and there are few homologous series in which these constants have been determined for many members. However, I have obtained a sufficient number of trustworthy determinations to show some results, which seem to be worth recording.

The amount of heat absorbed by one cc. of vapor (reduced to 0° and 760 mm. pressure) in the passage of the liquid to the gaseous state, is taken as the standard for comparison. This constant is found by the formula

$$L = \frac{H \times w}{W}.$$

where L = the heat of vaporization in one cc. of vapor,
W = the weight of one cc. of the liquid at its boiling-point,
H = the heat of vaporization,
and w = the weight of one cc. of the vapor at 0° and 760 mm. pressure.

Until the latent heat researches made by R. Schiff[1] these constants were determined without any special reference to the relationship of the compounds to one another, and, therefore, not many series can be found complete enough to make a comparison. I believe, however, that I have gathered the data quite completely and I give in this paper all the series in which the data are complete for as many as three members.

In the following tables the columns marked

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[1] *Ann. Chem.* (Liebig), **234**, 338. *1886.*

D = the vapor density,
B. P. = Boiling-point in absolute temperature,
S. G. = Specific gravity at the boiling-point,
H. V. = Heat of vaporization in calories,
V = Volume of vapor, in cubic centimeters (reduced to 0° and 760 mm. pressure), produced from one cc. of liquid at the boiling-point.
L = Heat of vaporization in a unit of volume (one cc.) of gas reduced to 0° and 760 mm. pressure.

The specific gravity of liquids at the boiling-point is taken from Clarke's tables of "Constants of Nature," where the references are fully given. The boiling-point is obtained from Carnelley's tables.

I will first show the results obtained from some of the fatty acids and their alkyl compounds.

FORMATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Formic acid	$HCHO_2$	23	373.8	1.1175	120.72[1]	542.26	0.2226
Methyl formate	CH_3CHO_2	30	305.3	0.95196	117.10[2] 102.70[3]	354.15	0.3306 0.2900
Ethyl formate	$C_2H_5CHO_2$	37	326.5	0.86667	92.15[4]	263.36	0.3499
Propyl formate	$C_3H_7CHO_2$	44	354.2	0.82146	85.25[4]	208.37	0.4091
Isobutyl formate	$C_4H_9CHO_2$	51	371.0	0.7784	77.0[4]	170.34	0.4520
Isoamyl formate	$C_5H_{11}CHO_2$	58	397.0	0.7554	71.65[4]	145.35	0.4929

Fig. 1 represents the curves of the formates, the density and boiling-point curves being shown on the same sheet. In all cases the corresponding acids fall in line in the density curves but not in the boiling-point curves. The acids, however, form both density and boiling-point curves of their own, as will be shown later on.

It will be seen from Fig. 1 that the heat of vaporization per unit of volume (H. V.) of methyl formate obtained from the result of Andrews' determination is too high. To conform to the curve it should be 0.2900 which would give 102.70 as the heat of vaporization (H. V.) instead of 117.10 as given by Andrews, whose determination has never been verified. But

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[1] Favre and Silbermann: *Ann. chim. phys.* [3], 37, 464-470.
[2] Andrews: Chem. Soc. Quar. J., 1, 27.
[3] Calculated from the data furnished by the curves shown in this paper.
[4] Schiff: *Ann. Chem.* (Liebig), 234, 338.

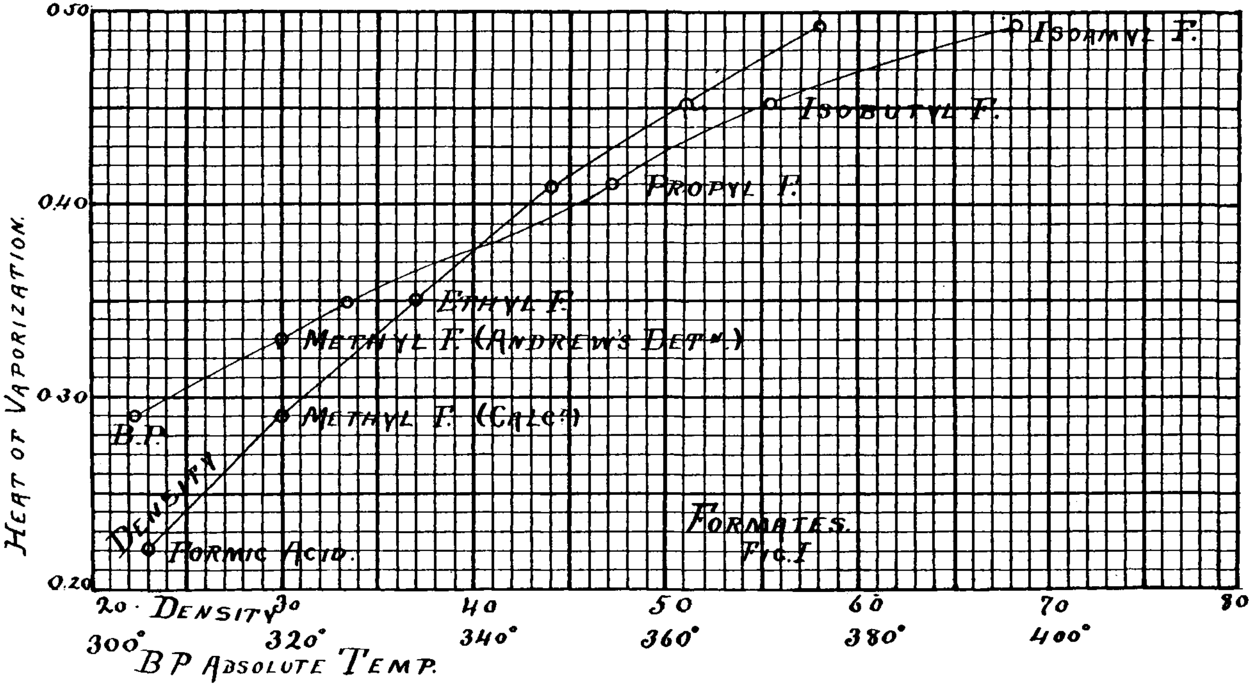
0.50
0.40
0.30
0.20
Heat of Vaporization.
Isoamyl F.
Isobutyl F.
Propyl F.
Ethyl F.
Methyl F. (Andrew's Detn.)
Methyl F. (Calcd.)
B.P.
Density
Formic Acid.
Formates.
Fig. I
20 · Density
30
40
50
60
70
80
300°
320°
340°
360°
380°
400°
B P Absolute Temp.

Fig. 1.

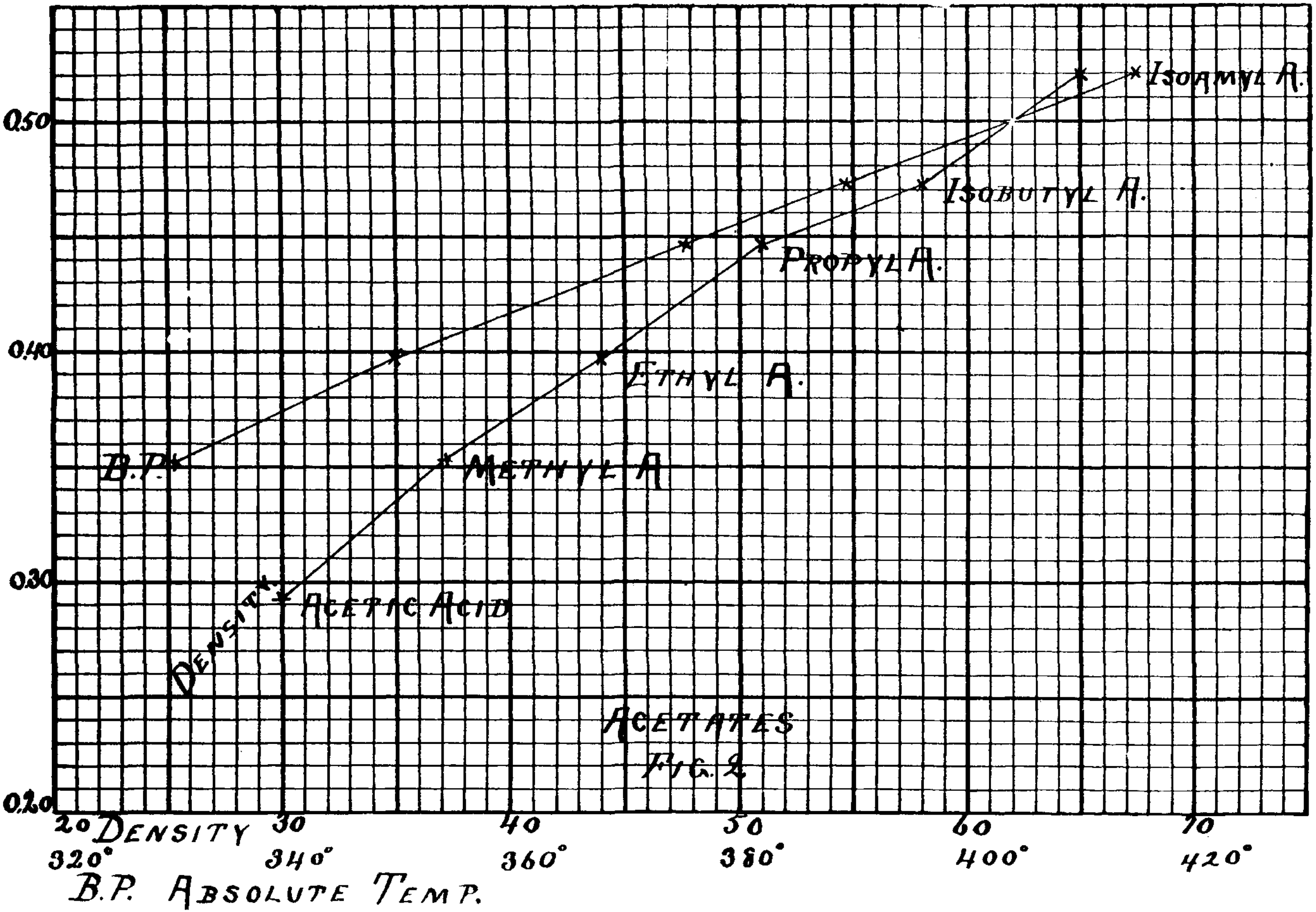
0.50
0.40
0.30
0.20
Isoamyl A.
Isobutyl A.
Propyl A.
Ethyl A.
Methyl A.
B.P.
Density
Acetic Acid
Acetates
Fig. 2
20 Density 30 40 50 60 70
320° 340° 360° 380° 400° 420°
B.P. Absolute Temp.

Fig. 2

since many of Andrews' determinations have been found by later investigators to be considerably too high, it is reasonable to suppose under the circumstances that this one is too high also. To substantiate this I will give the following instances, which may be cited from determinations made by Andrews and Schiff :

Methyl acetate	Andrews,	110.20
	Schiff,	93.90–94.0
Ethyl acetate	Andrews,	92.68
	Schiff,	83.0–83.1–83.1
Ethyl formate	Andrews,	105.30
	Schiff,	92.2–92.1

ACETATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Acetic acid	$HC_2H_3O_2$	30	391.1°	0.9372	101.91[1]	348.66	0.2923
Methyl acetate	$CH_3C_2H_3O_2$	37	330.3°	0.8808	93.95[2]	265.68	0.3536
Ethyl acetate	$C_2H_5C_2H_3O_2$	44	350.0°	0.82673	83.1[2]	209.70	0.3961
Propyl acetate	$C_3H_7C_2H_3O_2$	51	375.3°	0.7917	77.3[2]	173.25	0.4462
Isobutyl acetate	$C_4H_9C_2H_3O_2$	58	389.8°	0.7708	69.9[2]	148.32	0.4713
Isoamyl acetate	$C_5H_{11}C_2H_3O_2$	65	415.0°	0.74295	66.35[2]	127.56	0.5201

The acetates form very good curves, as will be seen in Fig. 2. The boiling-point curve is almost a straight line. It has been shown above that Schiff's determinations of the heats of vaporization (H. V.) of methyl and ethyl acetates are much lower than those of Andrews. Favre and Silberman's determination gives a number for ethyl acetate much higher than that of either of the other investigators, it being 105.8. The results of Schiff are taken as being more nearly correct.

PROPIONATES.

Name.		Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Propionic acid		$H.C_3H_5O_2$	37	413.7°	0.8589	90.42[3]	259.08	0.3490
Methyl propionate		$CH_3.C_3H_5O_2$	44	353.0°	0.836798	84.15[4]	212.25	0.3965
Ethyl	"	$C_2H_5.C_3H_5O_2$	51	371.7°	0.7962	77.1[4]	174.64	0.4415
Propyl	"	$C_3H_7.C_3H_5O_2$	58	395.6°	0.76815	71.5[4]	147.81	0.4832
Isobutyl	"	$C_4H_9.C_3H_5O_2$	65	409.8°	0.74424	66.0[4]	127.78	0.5165
Isoamyl	"	$C_5H_{11}.C_3H_5O_2$	72	433.5°	0.7295	63.05[4]	113.08	0.5576

The curves representing the propionates are shown in Fig. 3, and it will be seen that they are quite regular. The heat of vaporization (H. V.) of propionic acid has never been deter-

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[1] Favre and Silberman : *Ann. chim. phys.* [3], 37, 464-470.

[2] Schiff : *Ann. Chem.* (Liebig), 234, 338.

[3] Calculated by the data furnished by the curves shown in this paper.

[4] Schiff : *Ann Chem.* (Liebig), 234, 338.

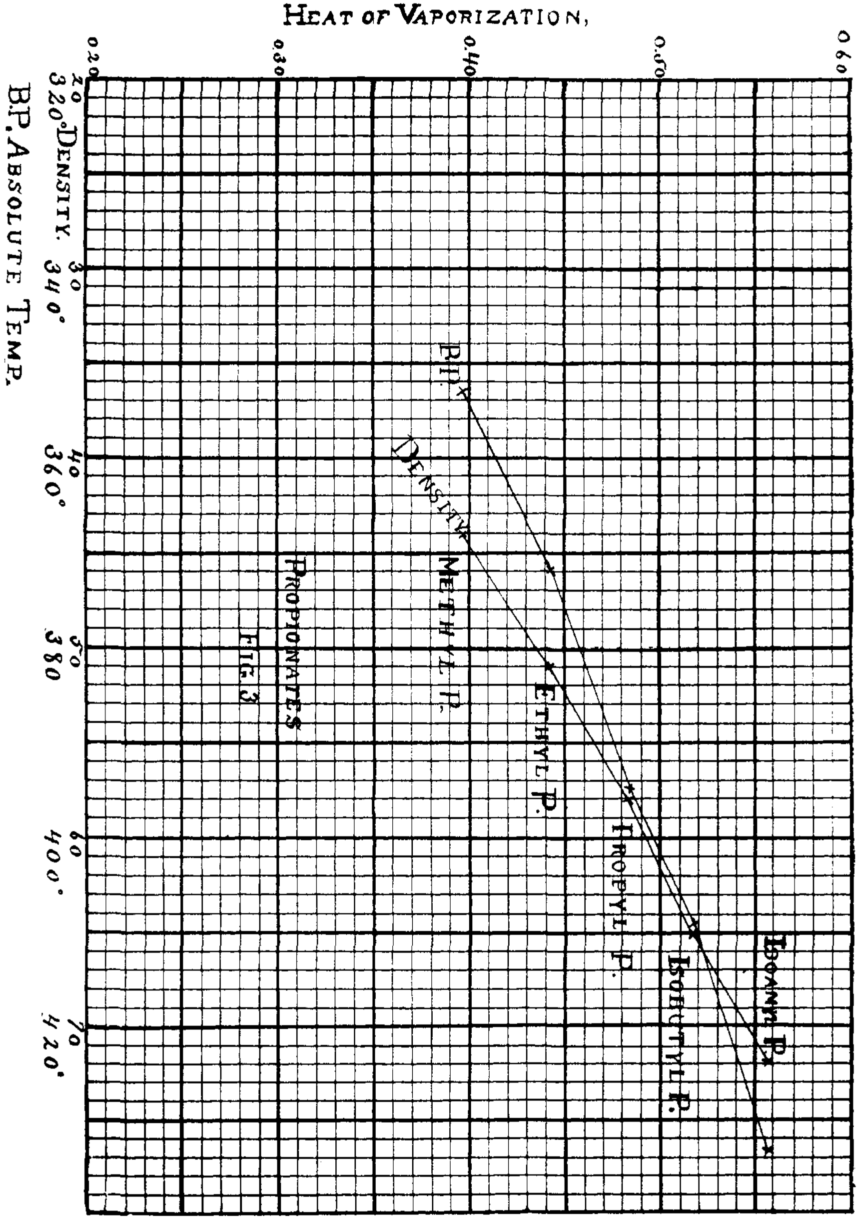
HEAT OF VAPORIZATION,
0.20
0.30
0.40
0.50
0.60
20
30
40
50
60
70
DENSITY.
320°
340°
360°
380
400°
420°
B.P. ABSOLUTE TEMP.
B.P.
DENSITY
METHYL P.
ETHYL P.
PROPYL P.
ISOBUTYL P.
ISOAMYL P.
PROPIONATES
FIG. 3

FIG. 3.

mined; but according to the density curve of the propionates, its heat per unit of volume of vapor (L.) should be 0.3490, which would give for the heat of vaporization (H. V.) the number 90.42.

BUTYRATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Butyric acid	$H.C_4H_7O_2$	44	435.5°	0.8120	114.67[1] 82.79[2]	205.96	0.5567 0.4020
Methyl butyrates	$CH_3C_4H_7O_2$	51	375.3°	0.80261	87.93[1] 77.25	175.64	0.4972 0.4398
Ethyl "	$C_2H_5C_4H_7O_2$	58	392.0°	0.7694	71.5[3]	148.05	0.4829
Propyl "	$C_3H_7C_4H_7O_2$	65	416.4°	0.745694	66.2[3]	128.03	0.5170
Isobutyl "	$C_4H_9C_4H_7O_2$	72	429.7°	0.7163	61.9[3]	111.03	0.5575
Isoamyl "	$C_5H_{11}C_4H_7O_2$	79	451.0°	0.71148	59.4[3]	100.51	0.5910

The curves of the butyrates are shown in Fig. 4. The density curve is almost a straight line, while the boiling-point curve breaks badly at propyl butyrate. This would indicate that its boiling-point, as determined, is too high and should be 408° (absolute temperature) instead of 416.4°, as determined by Linneman, which is given the preference by Carnelley over other determinations. The recorded results of the determinations of the boiling-point of propyl butyrate are as follows:

144.3° C.	Pawlewski.
143.42° C.	Linneman.
142.7° C.	Elsässer.
139°–141° C.	Chancel.
137.25° (765)	Pierre and Puchot.

The last result would agree very well with that deduced from the curve, *viz.*, 135° C.

The heat of vaporization (H. V.) of butyric acid has only been determined by Favre and Silberman. Their result is 114.67 cal., which is probably too high. It gives the heat per unit of volume (L.) 0.5567, which throws it entirely out of the curve shown in Fig. 4, according to which the number should be about 0.4020; this would give 82.79 cal. as the heat of vaporization (H. V.) of butyric acid. As will be seen in the table above Favre and Silberman's result for methyl butyrate is much higher than Schiff's.

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[1] Favre and Silberman: *Ann. chim. phys.* [3], **37**, 464-470.

[2] Calculated by the data furnished by the curves shown in this paper.

[3] Schiff: *Ann. Chem.* (Liebig). **234**, 338.

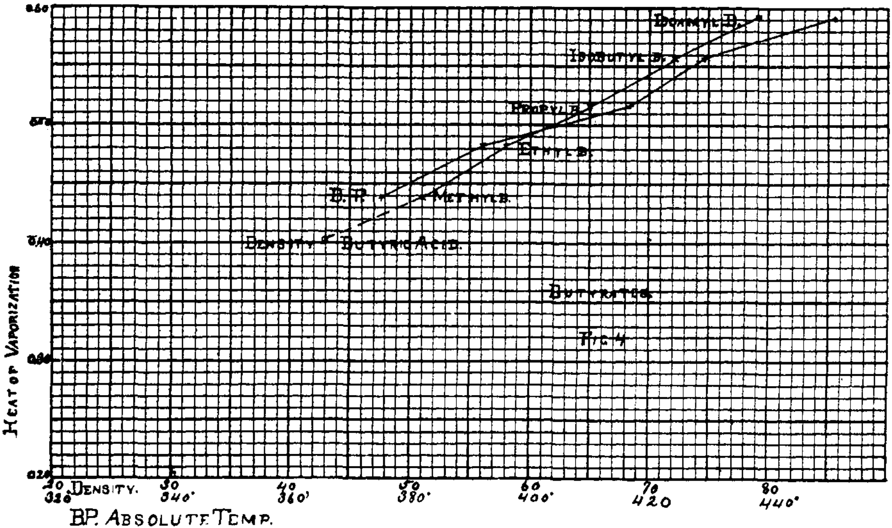
Isoamyl B.
Isobutyl B.
Propyl B.
Ethyl B.
B.P.
Methyl B.
Density of Butyric Acid.
Butyrates.
Fig. 4.
Heat of Vaporization
0.60
0.50
0.40
0.30
0.20
20 Density.
30
40
50
60
70
80
320
340°
360°
380°
400°
420
440°
B.P. Absolute Temp.

FIG. 4.

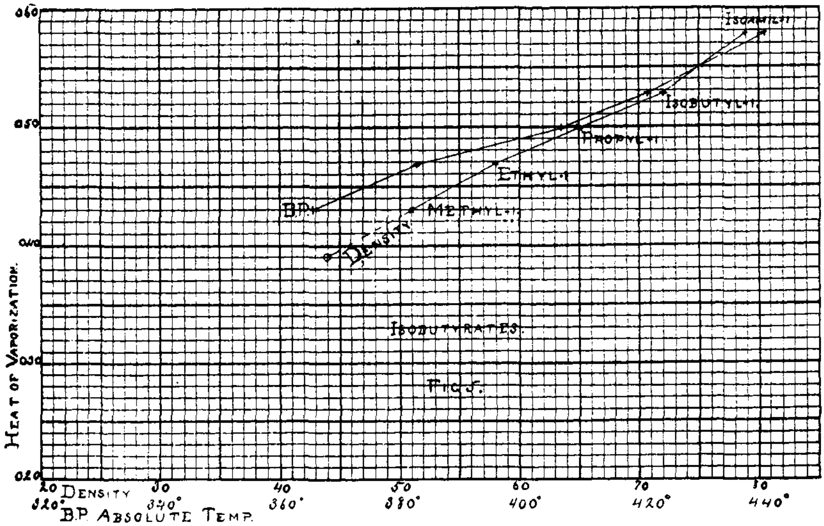
Isoamyl-I.
Isobutyl-I.
Propyl-I.
Ethyl-I.
B.P.
Methyl-I.
Density
Isobutyrates.
Fig. 5.
Heat of Vaporization.
0.60
0.50
0.40
0.30
0.20
20 Density
30
40
50
60
70
80
320°
340°
360°
380°
400°
420°
440°
B.P. Absolute Temp.

FIG. 5.

ISOBUTYRATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Isobutyric acid	$H.C_4H_7O_2$	44	428.5°	0.8054	76.67[1]	204.29	0.3900
Methyl isobutyrate	$CH_3.C_4H_7O_2$	51	365.5°	0.80397	75.5[2]	175.93	0.4291
Ethyl "	$C_2H_5.C_4H_7O_2$	58	383.0°	0.7681	69.2[2]	147.80	0.4682
Propyl "	$C_3H_7.C_4H_7O_2$	65	407.0°	0.74647	63.9[2]	128.17	0.4985
Isobutyl "	$C_4H_9.C_4H_7O_2$	72	421.6°	0.73281	59.95[2]	113.59	0.5278
Isoamyl "	$C_5H_{11}C_4H_7O_2$	79	441.0°	0.70662	57.65[2]	99.82	0.5775

The isobutyrate curves (Fig. 5) seem to indicate that the heats of vaporization (H.V.) of the propyl and isobutyl isobutyric rates as determined are a trifle too low. From the density curve it will be seen that the heat per unit of volume (L.) of isobutyric acid should be 0.3900 which would give 76.67 cal. for the heat of vaporization (H. V.). No determination of this constant has been recorded.

VALERATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Valeric acid	$H.C_5H_9O_2$	51	458.4°	0.7828	103.52[3] 73.83[4]	171.30	0.6042 0.4310
Methyl valerate	$CH_3C_5H_9O_2$	58	389.3°	0.77518	69.95[5]	149.16	0.4684
Ethyl "	$C_2H_5C_5H_9O_2$	65	407.0°	0.74764	64.65[6]	128.37	0.5036
Propyl "	$C_3H_7C_5H_9O_2$	72	428.5°	0.727405	61.2[5]	112.75	0.5427
Isobutyl "	$C_4H_9C_5H_9O_2$	79	442.0°	0.70549	57.85[5]	99.66	0.5805
Isoamyl "	$C_5H_{11}C_5H_9O_2$	86	460.5°	0.698435	56.2[5]	90.64	0.6200

The curves representing the valerates are shown in Fig. 6. The density curve is quite uniform. Schiff finds the heat of vaporization (H. V.) of isoamyl valerate to be 56.2 cal. and from the curve it will be seen that the heat per unit of volume (L.) should be 0.6200, but this constant could not be calculated since no determination of the specific gravity of this compound at its boiling-point has been made. However, assuming the curve to be correct, the specific gravity at the boiling-point becomes 0.698435. The only determination of the heat of vaporization (H. V.) of valeric acid on record is that of Favre and Silberman, which places it at 103.52 cal. This would give 0.6042 as the heat per unit of volume (L.), while according to the curve it should be 0.4310, which gives 73.83 cal. as the heat of vaporization (H. V.).

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[1] Calculated by the data furnished by the curves shown in this paper.

[2] Schiff: *Ann. Chem.* (Liebig), **234**, 238.

[3] Favre and Silbermau: *Ann. chim. phys.* [3]. 37. 464-470.

[4] Calculated by the data furnished by the curves shown in this paper.

[5] Schiff: *Ann. Chem.* (Liebig), **234**. 338.

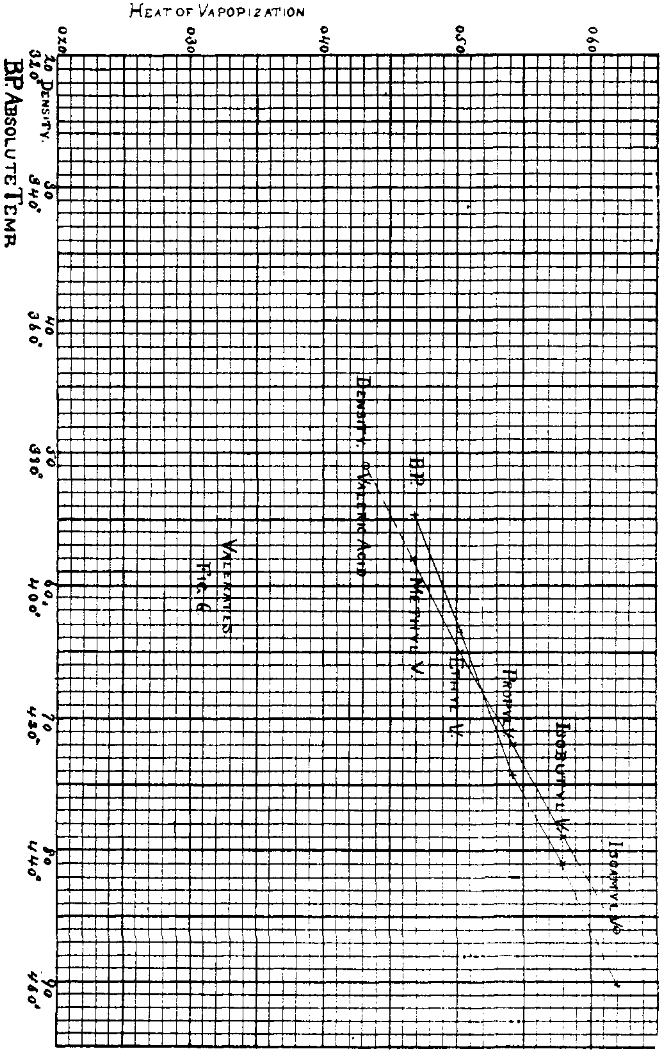
HEAT OF VAPOPIZATION
020
030
040
050
060
20 DENSITY.
310°
B.P. ABSOLUTE TEMR
30
340°
40
360°
50
380°
60
400°
70
430°
80
440°
90
460°
DENSITY. OF VALERIC ACID
B.P.
METHYL V.
ETHYL V.
PROPYL V.
ISOBUTYL V.
ISOAMYL V.
VALERATES
FIG. 6

FIG. 6.

According to the boiling-point curve the boiling-point of propyl valerate 428.5° (absolute temperature) or 155.5° C. is a trifle too high.

Fig. 7 gives all of the density curves of the compounds above mentioned, in one diagram, showing that the relationship between them is very close and that the uniformity of the curves is very striking.

Fig. 8 is a similar combination of the boiling-point curves, showing the general tread of them to be almost that of a straight line.

ACIDS.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Formic	$H.CHO_2$	23	373.8°	1.1175	92.71[1] 120.72[2]	542.26	0.2659 0.2226
Acetic	$H.C_2H_3O_2$	30	391.1°	0.9372	101.91[2]	348.66	0.2923
Propionic	$H.C_3H_5O_2$	37	413.7°	0.8589	90.42[3]	259.08	0.3490
Isobutyric	$H.C_4H_7O_2$	44	428.5°	0.8054	79.67[3]	204.29	0.3900
Butyric	$H.C_4H_7O_2$	44	435.5°	0.8120	82.79[3]	205.96	0.4020
Valeric	$H.C_5H_9O_2$	51	458.4°	0.7828	73.83[3]	171.30	0.4310

The curves of the acids (Fig. 9) are constructed as far as possible from their constants, as determined and recorded by the various observers, but otherwise the data used have been derived from the curves formed by their corresponding compounds.

The heat of vaporization (H. V.) of acetic acid as determined by Ramsey and Young seems to be too low as it does not conform to either the density or boiling-point curve.

ALCOHOLS.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Water	$H.OH$	9	373.0°	0.9589	536.0[4]	1189.11	0.4507
Methyl alcohol	CH_3OH	16	339.2°	0.7483	263.86[2]	521.97	0.5055
Ethyl "	C_2H_5OH	23	351.3°	0.74035	201.42[5]	359.25	0.5607
Isopropyl "	C_3H_7OH	30	355.8°	0.7413	159.72[5]	275.78	0.5791
Propyl " (nor.)	C_3H_7OH	30	370.1°	0.7366	164.07[5]	274.03	0.5987
Isobutyl "	C_4H_9OH	37	381.4°	0.7265	136.16[5]	219.14	0.6213
Butyl " (nor.)	C_4H_9OH	37	389.96°	0.7269	138.18[5]	219.26	0.6298
Amyl "	$C_5H_{11}OH$	44	404.4°	0.7154	118.15[5]	181.46	0.6511

[1] Ramsey and Young : *J. Chem. Soc.*, Lond., 49, 790.

[2] Favre and Silberman : *Ann. chim. phys.* [3], 37, 464-470.

[3] Calculated by the data furnished by the curves shown in this paper.

[4] Regnault : Mem. Acad. Sci., 21, 638.

[5] Louguiuine : *Compt. rend.*, 119, 601.

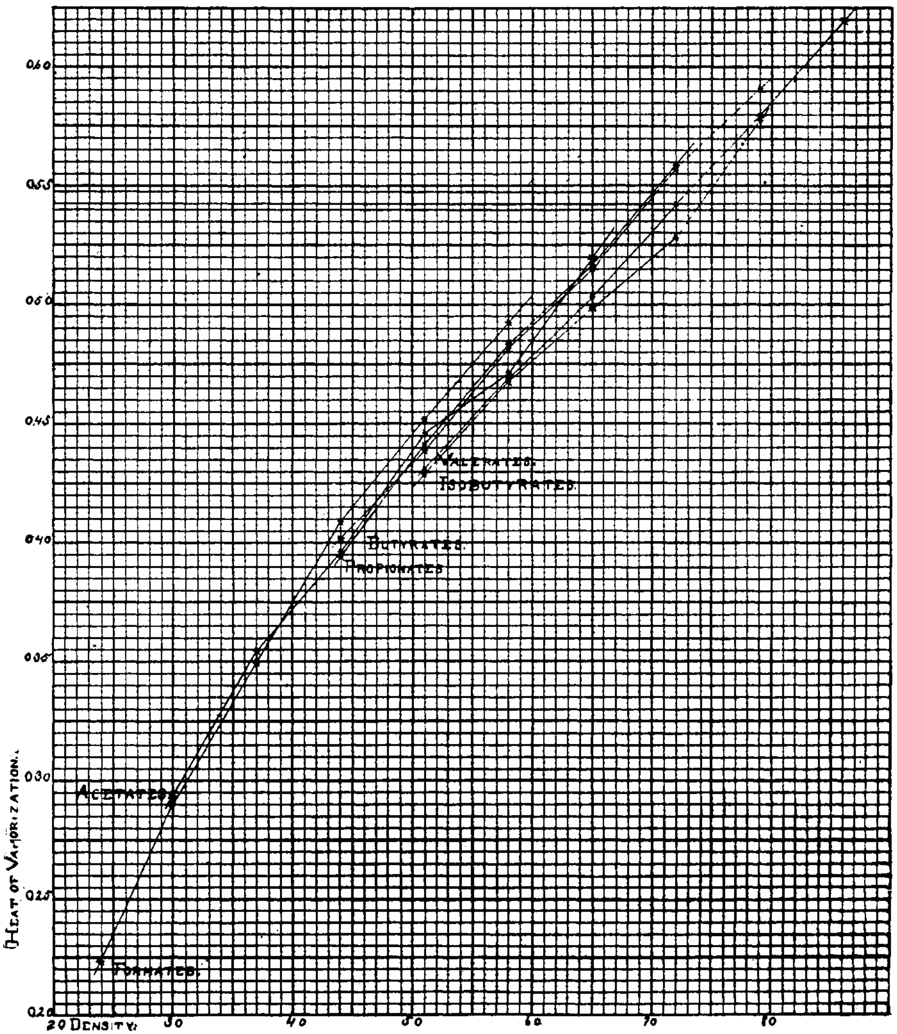
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
Heat of Vaporization.
20 Density.
30
40
50
60
70
80
Formates.
Acetates.
Propionates
Butyrates.
Isobutyrates.
Valerates.

FIG. 1.

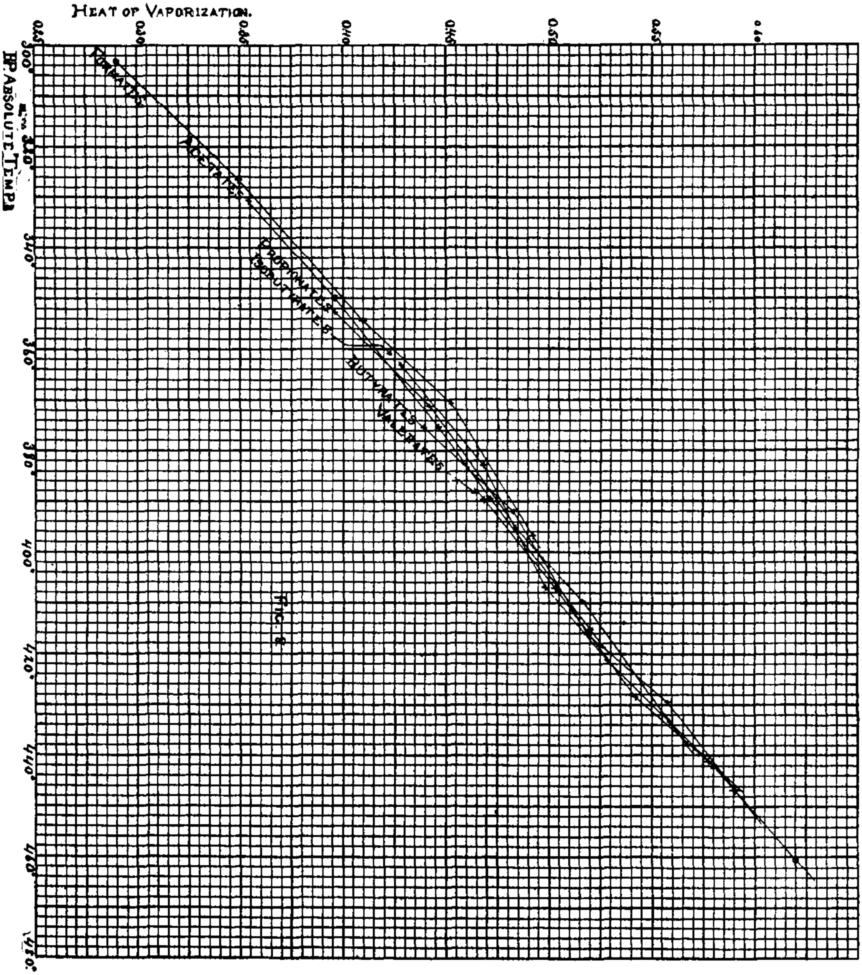
Heat of Vaporization.
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
H.P. Absolute Temp.
300°
320°
340°
360°
380°
400°
420°
440°
460°
480°
Formates
Acetates
Propionates
Isobutyrates
Butyrates
Valerates
Fig. 8

FIG. 8.

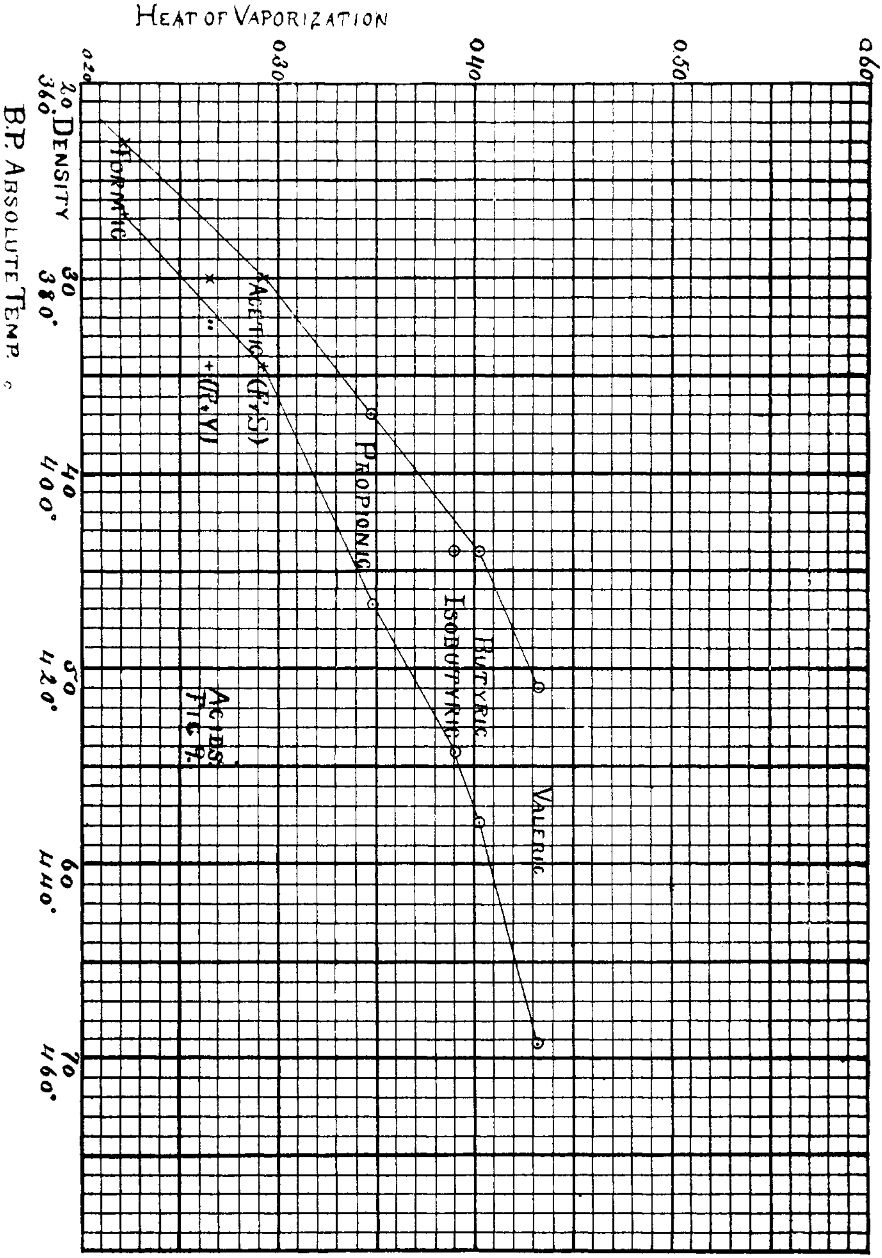
HEAT OF VAPORIZATION
0.20
0.30
0.40
0.50
0.60
DENSITY
20
30
40
50
60
70
B.P. ABSOLUTE TEMP.
360°
380°
400°
420°
440°
460°
FORMIC
ACETIC (F+S)
" (R+Y)
PROPIONIC
BUTYRIC
ISOBUTYRIC
VALERIC
ACIDS.
FIG. 9.

FIG. 9.

The normal alcohols form quite symmetrical curves, as is shown in Fig. 10. In the density curve, water, as the type, falls in with the alcohols as the acids do with their corresponding compounds. It will be noticed that isopropyl and isoamyl alcohols do not fall into line with the normal alcohols, but, as might be expected, they form a portion of a curve for which the data relating to the remaining members of the series are not to be had at present.

In constructing the alcohol curves, the heat of vaporization (H. V.) of methyl alcohol, as determined by Favre and Silberman, was taken in preference to that of Diakonoff, which is believed to be an impossible value. These determinations are as follows:

Favre and Silberman	263.86 cal.
Diakonoff	123.79 "

In the case of ethyl alcohol the determination of Longuinine was used, although three determinations are recorded as follows:

Favre and Silberman	208.92 cal.
Andrews	202.40 "
Longuinine	201.42 "

Of the two determinations of propyl alcohol (normal)

Diakonoff	165.92 cal.
Longuinine	164.07 "

I have made use of the latter.

Two determinations of amyl alcohol (by fermentation) are recorded, *viz.*

Favre and Silberman	121.37 cal.
Longuinine	118.15 "

and I have used the latter.

The determinations of the other alcohols given in the above table have been made only by Longuinine.

HYDROCARBONS.

Sufficient data has been found to make it possible to construct curves for a portion of the C_nH_{2n-6} series of the hydrocarbons, as follows:

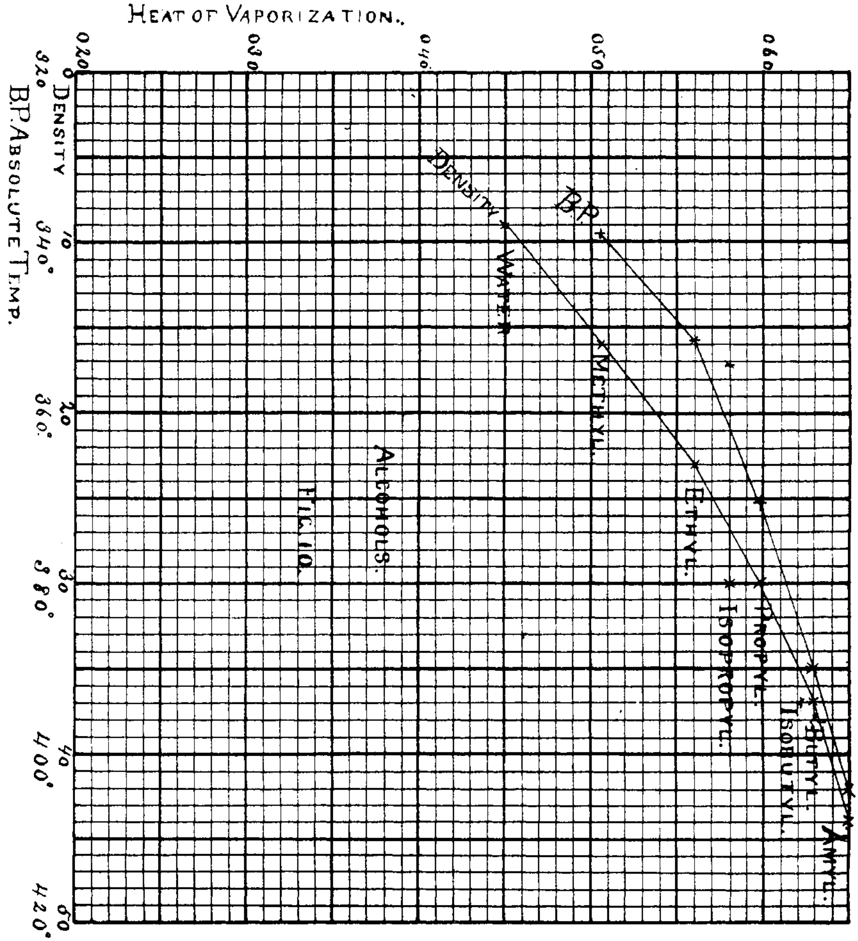
Heat of Vaporization.
020
030
040
050
060
0
10
20
30
40
50
Density
320
340°
360°
380°
400°
420°
B.P. Absolute Temp.
Density
B.P.
Water
Methyl.
Ethyl.
Propyl.
Isopropyl.
Butyl.
Isobutyl.
Amyl.
Alcohols.
Fig. 10.

FIG. 10.

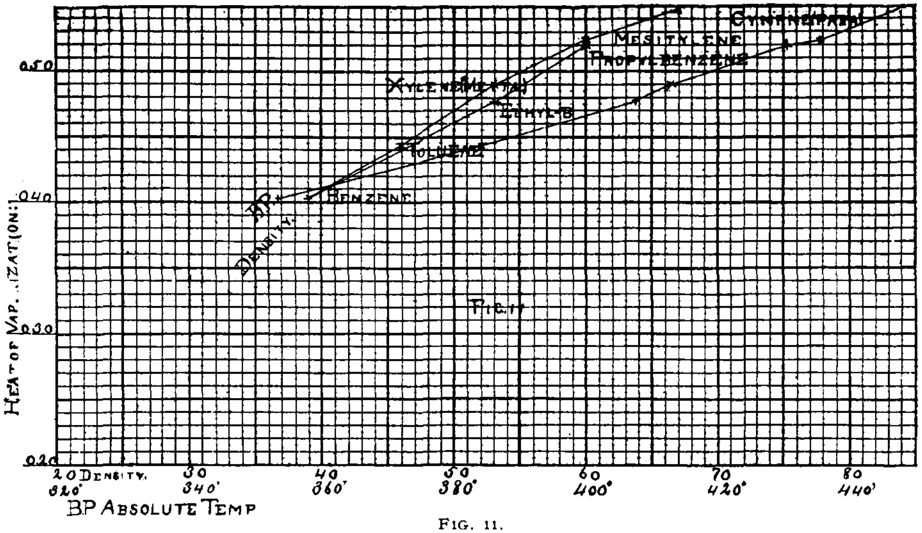

FIG. 11.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Benzene	C_6H_6	39	353.35[5]	0.8111	93.45[4]	232.11	0.4026
Toluene	C_7H_8	46	383.8[5]	0.77694	83.55[4]	188.49	0.4432
Ethyl benzene	C_8H_{10}	53	407.7[5]	0.7612	76.4[4]	160.29	0.4766
Xylene (meta)	C_8H_{10}	53	412.9[5]	0.75715	78.25[4]	159.44	0.4908
Propyl benzene	C_9H_{12}	60	430.2[5]	0.7399	71.75[4]	137.63	0.5213
Mesitylene	C_9H_{12}	60	435.7[5]	0.7372	71.75[4]	137.12	0.5232
Cymene	$C_{10}H_{14}$	67	448.0[5]	0.7248	66.3[4]	120.73	0.5491

As will be seen in Fig. 11 these hydrocarbons form two density curves ; one is formed by benzene, ethyl benzene, and propyl benzene. and the other by benzene, toluene, xylene, mesitylene, and cymene. The boiling-point curve is fairly regular and contains all of the series.

CONCLUSION.

From the foregoing we may enunciate the following law, *viz.* : "In any homologous series, the heat of vaporization in a unit of volume of the vapor, under the same conditions as to temperature and pressure, is proportional to the density and also to the absolute boiling-point."

It will be noticed that the acid radical in any series fixes the

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[4] Schiff : *Ann. chem.* (Liebig), 234, 338.

characteristic of the curve, *i. e.*, the acid radical is the basis of the structure of the molecule, and the bases in combination with it, do not alter the general molecular architecture.

When more complete data have been obtained some interesting developments in this direction may be expected.

VANDERBILT UNIVERSITY.

THE DETERMINATION OF METHANE AND HYDROGEN BY EXPLOSION.[1]

BY AUGUSTUS H. GILL AND SAMUEL P. HUNT.[2]

Received September 26, 1895.

IN making an analysis of illuminating gas by Hempel's method it was noticed that the determination of the constituents by explosion was by no means as accurate as that made by absorption. This had been observed by Hinman[3] and is probably due (1) to the fact that an aliquot part of the residue (after all absorptions had been made) containing the methane and hydrogen is used, necessitating the multiplication of errors by a factor as large as four or five, and (2) to the possible absorption of the carbon dioxide formed by the water in the burette. To obviate these difficulties, it was determined to use all the gas left after the absorptions had been made, mercury as the confining liquid and to explode with pure oxygen rather than with air. Instead of using the gas left after the actual absorptions, which would be of unknown composition and troublesome to obtain, an artificial mixture, made from methane, hydrogen and nitrogen, approximating closely to the composition of the residue, was employed.

Preparation of the Gaseous Mixtures.—The hydrogen was prepared by the electrolysis of water; it was then shaken up with potassium pyrogallate to remove the slight quantity of oxygen with which it was mixed. and upon analysis was found to contain four and two tenths per cent. of nitrogen. In making an analysis of hydrogen, we would lay especial emphasis upon the necessity of having the ratio of explosive mixture to inert gases as great as 1 : 6 as Hempel[4] recommends, in order not to burn the nitrogen.

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[1] Prepared for the Springfield Meeting, August 28, 1895.

[2] The work described in this paper formed the basis of a thesis presented by Mr. Hunt to the Faculty of the Massachusetts Institute of Technology for the Degree of Bachelor of Science.

[3] Massachusetts Senate Document No. 16, 1892. Inspection of Gas and Gas Meters, p. 12.

[4] Hempel. "Gasanalytische Methoden" p. 132