LXXIV.—A New Formula for the Latent Heat of Vapours.*

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THE most general formula for the latent heat of vaporisation is that of Clausius and Clapeyron,

$$L = t(v_2 - v_1) \frac{\delta p}{\delta t}.$$

v_2 and v_1 being the molecular volumes of the vapour and liquid respectively, t the absolute temperature, and p the pressure of the saturated vapour. L is, of course, the value of the heat of vaporisation in mechanical units. The only assumptions made in the deduction of the formula are the two thermodynamical principles. It is therefore applicable to all changes of state, and contains no special assumptions as to the structure of matter.

If, however, definite postulates are made as to the internal structure of matter, it becomes possible to deduce formulæ correlating the variables in terms of which the state of the matter can be expressed. The most successful of such formulæ is that of van der Waals for liquids and vapours,

$$\left(p + \frac{a}{v_2}\right)(v - b) = Rt.$$

By the elimination of one of the variables from such a characteristic equation and the above general thermodynamical equation, the latent heat can be expressed in terms of two independent variables only.

A formula of this kind has been deduced by Bakker (*Zeitsch. physikal. Chem.*, 1895, **18**, 519). It is

$$L = Rt \log_e \frac{v_2 - b}{v_1 - b}.$$

Although the formula has been derived by rigid reasoning solely from van der Waals' equation and the thermodynamical principles, it is not in agreement with the facts, the calculated values for the latent heats being in most cases more than 20 per cent. below the experimentally determined magnitudes. Van der Waals' equation is not, therefore, a sufficiently close approximation to the truth to enable the latent heats to be calculated from it with a satisfactory degree of accuracy.

* To avoid constant repetition we may state at once that the symbols employed in the formulæ occurring in this paper always refer to gram-molecules, and that to avoid the use of J , heat is supposed to be measured in mechanical units.

Bakker's formula can also be deduced from the simplified characteristic equation

$$\pi(v-b) = R t,$$

where π is the total pressure, that is, the sum of the internal and external pressures, and therefore the discrepancy cannot arise from incorrect assumptions as to the magnitude of the internal pressure. Perhaps it is not legitimate to assume that b is constant. This conjecture is supported by the circumstance that, although for all substances with polyatomic molecules the formula gives a value of the heat of vaporisation which is too low, for mercury vapour the calculated and experimental values of the latent heat are in good agreement, for it might reasonably be expected that the variation of b would be least in the case of substances composed of monatomic molecules.

We shall accordingly assume that b is a variable the magnitude of which depends on the temperature, and investigate how closely such an assumption will bring theory and practice into conformity with one another. Suppose that small amounts of the substance are transferred successively from the interior of the liquid to that of the gas, the movement from the liquid to the gaseous phase being so slow that the moving portion of matter always assumes the precise condition of its immediate surroundings. (The change in state across the interface of the liquid and gas is conceived as continuous, the internal pressure and density diminishing gradually as the boundary is crossed.) Let a gram-molecule of the liquid be thus transformed into vapour. The heat absorbed during this process is

$$\int_{v_1}^{v_2} \frac{\delta H}{\delta v} dv,$$

v_2 being the molecular volume of the vapour, and v_1 that of the liquid.

But
$$\frac{\delta H}{\delta v} = t \frac{\delta \pi}{\delta t},$$

where π is the total pressure, namely, the sum of the internal and external pressures. Therefore the total heat absorbed, or the molecular latent heat, is given by

$$\int_{v_1}^{v_2} t \frac{\delta \pi}{\delta t} dv;$$

$\frac{\delta \pi}{\delta t}$ can be found from the characteristic equation

$$\pi(v-b) = R t;$$

for, by differentiation, we obtain

$$\frac{\delta \pi}{\delta t}(v-b) - \pi \frac{db}{dt} = R,$$

and therefore

$$\begin{aligned}\frac{\delta\pi}{\delta t} &= \frac{R}{v-b} + \pi \frac{db}{dt} \cdot \frac{1}{v-b} \\ &= \frac{R}{v-b} + \frac{Rt}{(v-b)^2} \frac{db}{dt} \\ \therefore \int_{v_1}^{v_2} \frac{\delta\pi}{\delta t} dv &= L = Rt \log_e \frac{v_2-b}{v_1-b} + Rt^2 \left(\frac{1}{v_1-b} - \frac{1}{v_2-b} \right) \frac{db}{dt}. \quad (A)\end{aligned}$$

If the values of v_1 , v_2 , and L are known for a series of definite temperatures, it is obviously possible to estimate the values of b and $\frac{db}{dt}$ corresponding with each definite temperature from the above equation. This has been done for several compounds, and it has been found that for those examined, $\frac{db}{dt}$ is approximately constant over a wide range of temperature.

As it may be assumed that $\frac{db}{dt}$ is constant, the only information which is needed in order to fix the value of b for any given temperature is a knowledge of the value of b at the critical point, and also the magnitude of $\frac{db}{dt}$.

With the aid of the law of the rectilinear diameter and the relation discovered by J. E. Mills (*J. Physical Chem.*, 1905, **9**, 402), namely, that at the critical temperature $\frac{\delta p}{\delta t} = \frac{2R}{v_c}$, the value of b_c * and $\frac{db}{dt}$ can be calculated. We shall now deduce the formulæ required for this calculation, and give one example of their application.

From (A)

$$t(v_2 - v_1) \frac{\delta p}{\delta t} = L = Rt \log_e \frac{v_2-b}{v_1-b} + Rt^2 \left(\frac{1}{v_1-b} - \frac{1}{v_2-b} \right) \frac{db}{dt},$$

and therefore

$$t(v_2 - v_1) \frac{\delta p}{\delta t} = Rt \log_e \left(1 + \frac{v_2 - v_1}{v_1 - b} \right) + Rt^2 \frac{v_2 - v_1}{(v_1 - b)(v_2 - b)} \frac{db}{dt}.$$

At a temperature just below the critical point, $v_2 - v_1$ is small, and the above equation reduces to

$$\frac{\delta p}{\delta t} = R \left\{ \frac{1}{v_c - b_c} + \frac{1}{(v_c - b_c)^2} t \frac{db}{dt} \right\}.$$

* The suffix c is used to indicate that the symbol to which it is attached refers to a magnitude at the critical point.

With Mills' relation this becomes

$$\frac{2}{v_c} = \frac{1}{v_c - b_c} + \frac{1}{(v_c - b)^2} t_c \frac{db}{dt} \quad \dots \quad (i)$$

Since $\frac{db}{dt}$ is constant, we have

$$\frac{db}{dt} = \frac{b_c - v_0}{t_c} \quad \dots \quad (B)$$

v_0 being the extrapolated molecular volume of the liquid at the absolute zero of temperature.

On this value of $\frac{db}{dt}$ being substituted in (i), we find that

$$b_c = v_c \mp \sqrt{\frac{v_c(v_c - v_0)}{2}} \quad \dots \quad (C)$$

The negative sign must be taken, since b_c cannot be greater than v_c .

From the law of the rectilinear diameter, it can easily be shown that v_0 is given by the equation

$$v_0 = \frac{M}{\frac{t_c}{t_c - t}(\rho_1 + \rho_2 - 2\rho_c) + 2\rho_c} \quad \dots \quad (D)$$

M being the molecular weight, and ρ_1 and ρ_2 the densities of the liquid and vapour respectively at the temperature t . From the equations (B), (C), and (D), and the necessary experimental data, the values of b_c and $\frac{db}{dt}$ can without difficulty be calculated. From

these two magnitudes b can be found at any temperature.

As an example of the use of the foregoing formulæ, the calculation of the heats of vaporisation of fluorobenzene will be taken.*

v_0 is in the first place calculated from (D). The value of the first term in the denominator of the right-hand side of the equation is calculated for five temperatures 40° apart, and in calculating v_0 from the formula the mean of these values is taken. The numbers obtained are:

t .	ρ_1 .	ρ_2 .	$2\rho_c$.	t_c .	$\frac{t_c}{t_c - t}(\rho_1 + \rho_2 - 2\rho_c)$.
513	0.6789	0.08403	0.7082	559.6	0.65687
473	0.7671	0.04184	—	—	0.65071
433	0.8363	0.01992	—	—	0.65419
393	0.8955	0.00835	—	—	0.65728
353	0.9496	0.00288	—	—	0.66172
					Mean = 0.65615

v_0 then works out as equal to 70.363.

Substituting this value of v_0 in the equation

$$b_c = v_c - \sqrt{\frac{v_c(v_c - v_0)}{2}},$$

* All the experimental data for this communication are taken from a paper by S. Young (*Sci. Proc. Roy. Dubl. Soc.*, 1910, **12**, 414).

and taking v_c as being equal to 271.110, b_c is found to have the value 106.148.

$\frac{db}{dt}$ calculated from (A) is 0.06394.

It is obvious that, from a knowledge of the magnitude of b_c and $\frac{db}{dt}$, the value of b can be found for any desired temperature, and

that b and $\frac{db}{dt}$ being known, the heat of vaporisation can be calculated from equation (A) with the aid of Young's values of v_1 and v_2 .

In the following table the values of b and the calculated and observed values of the heats of vaporisation at intervals of 10° over a range of 200° is given.

TABLE I.
Fluorobenzene.

θ .	b .	L (calc.).	L (obs.).
80	92.934	79.76	80.07
90	93.573	79.08	78.59
100	94.214	77.21	77.10
110	94.853	74.98	75.05
120	95.492	73.24	73.03
130	96.132	72.02	71.02
140	96.771	69.27	68.75
150	97.410	67.35	66.48
160	98.050	65.39	64.37
170	98.689	63.09	62.37
180	99.329	61.08	60.17
190	99.968	58.10	57.82
200	100.608	55.84	55.35
210	101.247	53.27	53.04
220	101.887	50.34	50.37
230	102.526	47.19	47.38
240	103.165	43.77	44.07
250	103.805	39.43	40.29
260	104.444	35.21	35.65
270	105.083	29.47	29.54
280	105.723	19.95	20.82

The above method of calculation of v_0 is dependent on the validity of the law of the rectilinear diameter. It has been shown, however, by Young that the linear relation between the temperature and the sum of the densities of the liquid and saturated vapour is not quite exact. The values calculated by this method therefore contain a small error. Taking into account the slight curvature of the diameter, as given by Young's measurements, we obtain for fluorobenzene

$$v_0 = 69.635 \text{ and } \frac{db}{dt} = 0.06472.$$

In this case the correction is too small to influence to any marked degree the agreement between calculated and observed latent heats.

For the rest of the substances examined we have, in calculating v_0 , introduced the correction for the slight curvature of the diameter. It is only in the case of the associated substances that this correction is considerable.

The following tables contain the values of the latent heats calculated by this method and those obtained by Young from vapour-pressure measurements. The heats of vaporisation are in calories per gram.

TABLE II.

Non-associated Liquids.

n-Pentane, C_5H_{12} .^{*} $v_0 = 80.27$. $\frac{db}{dt} = 0.0892$.

θ	30	60	90	120	150	170	180	190
<i>L</i> (calc.)	86.02	79.98	72.73	64.06	52.34	42.09	35.30	24.51
<i>L</i> (obs.)	85.76	80.07	72.73	64.48	53.39	42.06	35.01	24.68

n-Hexane, C_6H_{14} . $v_0 = 93.58$. $\frac{db}{dt} = 0.09760$.

θ	60	90	120	150	180	210	220	230
<i>L</i> (calc.)	81.12	74.72	67.81	59.55	49.81	36.49	29.96	19.93
<i>L</i> (obs.)	80.82	75.51	69.29	61.03	50.93	37.29	30.37	19.73

n-Heptane, C_7H_{16} . $v_0 = 108.79$. $\frac{db}{dt} = 0.10701$.

θ	70	100	130	160	190	220	250	260
<i>L</i> (calc.)	82.13	75.66	68.33	61.23	53.34	43.52	29.02	20.77
<i>L</i> (obs.)	80.44	75.80	69.37	62.65	56.05	46.46	31.25	21.90

n-Octane, C_8H_{18} . $v_0 = 123.85$. $\frac{db}{dt} = 0.11732$.

θ	120	150	180	210	240	270	280	290
<i>L</i> (calc.)	73.82	66.62	59.57	52.04	42.92	31.50	25.96	17.87
<i>L</i> (obs.)	71.43	66.45	60.91	54.83	45.97	34.38	28.26	19.10

β -Methylbutane, C_5H_{12} . $v_0 = 79.95$. $\frac{db}{dt} = 0.08804$.

θ	10	40	70	100	130	160	170	180
<i>L</i> (calc.)	85.62	79.81	73.09	65.18	55.20	41.29	34.65	26.38
<i>L</i> (obs.)	84.73	79.12	71.95	64.83	55.07	41.27	34.28	24.65

$\beta\gamma$ -Dimethylbutane, C_6H_{14} . $v_0 = 92.69$. $\frac{db}{dt} = 0.09421$.

θ	50	80	110	140	170	200	210	220
<i>L</i> (calc.)	76.38	71.14	64.92	57.59	48.75	36.58	30.84	22.43
<i>L</i> (obs.)	77.90	72.64	65.83	58.45	49.36	37.15	31.09	22.14

* The values of the constants for *n*-pentane are obtained directly from equation (A) (p. 786) by a method of trial, without assuming either Mills' relation or the law of the rectilinear diameter.

TABLE II. (*continued*).*Non-associated Liquids.**βε-Dimethylhexane*, C_8H_{18} . $v_0 = 123.29$. $\frac{db}{dt} = 0.11788$.

θ	90	120	150	180	210	240	260	270
L (calc.)	70.52	64.56	58.23	51.80	44.27	34.74	25.67	18.25
L (obs.)	70.03	64.01	57.90	53.07	46.38	37.37	27.93	19.54

cycloHexane, C_6H_{12} . $v_0 = 79.00$. $\frac{db}{dt} = 0.07427$.

θ	80	110	140	170	200	230	260	270
L (calc.)	84.25	79.37	73.72	67.24	59.44	49.66	35.03	26.93
L (obs.)	86.72	81.11	74.24	67.26	59.37	49.98	35.16	26.72

Benzene. $v_0 = 65.19$. $\frac{db}{dt} = 0.06166$.

θ	70	100	130	160	190	220	250	280
L (calc.)	95.83	91.31	85.25	78.86	71.31	61.85	49.29	27.96
L (obs.)	96.70	91.41	84.74	78.94	71.76	62.24	49.47	27.43

Chlorobenzene. $v_0 = 79.69$. $\frac{db}{dt} = 0.06449$.

θ	130	160	190	220	240	250	260	270
L (calc.)	79.86	75.10	69.78	64.15	60.12	57.77	55.32	52.84
L (obs.)	74.24	71.26	67.37	62.89	59.49	57.50	55.15	52.56

Bromobenzene. $v_0 = 83.71$. $\frac{db}{dt} = 0.06392$.

θ	150	180	210	230	240	250	260	270
L (calc.)	61.58	57.94	54.02	51.46	49.92	48.55	47.01	45.35
L (obs.)	56.05	53.80	51.37	49.44	47.96	46.80	45.72	44.34

Iodobenzene. $v_0 = 90.05$. $\frac{db}{dt} = 0.06503$.

θ	180	200	220	240	250	260	270
L (calc.)	50.68	48.90	46.96	45.14	44.18	43.09	41.89
L (obs.)	46.69	45.80	44.78	43.27	42.43	41.40	40.29

Carbon tetrachloride. $v_0 = 70.43$. $\frac{db}{dt} = 0.06674$.

θ	70	100	130	160	190	220	250	280
L (calc.)	46.83	44.33	41.44	38.38	34.55	29.72	23.15	10.71
L (obs.)	46.77	44.15	40.98	37.95	34.04	29.45	23.19	10.43

Stannic chloride. $v_0 = 87.28$. $\frac{db}{dt} = 0.08239$.

θ	100	130	160	190	220	250	270	280
L (calc.)	31.35	29.41	27.33	25.13	22.52	19.28	16.82	15.34
L (obs.)	31.76	29.89	27.69	25.38	22.82	19.77	17.10	15.60

TABLE II. (*continued*).*Non-associated Liquids.**Ethyl ether.* $v_0=72.37$. $\frac{db}{dt}=0.08091$.

θ	0	30	60	90	120	150	180	190
L (calc.)	96.34	88.50	80.86	72.20	62.05	50.20	31.94	20.12
L (obs.)	92.52	85.18	78.44	70.97	62.24	51.09	31.87	19.38

Methyl formate, C₂H₄O₂. $v_0=43.59$. $\frac{db}{dt}=0.04793$.

θ	30	60	90	120	150	180	200	210
L (calc.)	119.84	109.65	99.32	87.94	74.62	57.43	40.77	25.41
L (obs.)	114.27	105.11	95.77	86.22	73.58	56.48	38.80	22.98

Ethyl formate, C₃H₆O₂. $v_0=57.89$. $\frac{db}{dt}=0.05922$.

θ	50	80	110	140	170	200	220	230
L (calc.)	96.76	89.18	81.15	72.25	61.62	48.19	34.32	23.66
L (obs.)	97.92	90.91	83.16	74.18	63.12	49.28	34.47	22.79

Methyl acetate, C₃H₆O₂. $v_0=57.82$. $\frac{db}{dt}=0.06080$.

θ	50	80	110	140	170	200	220	230
L (calc.)	107.22	97.04	86.92	76.12	64.14	49.24	34.62	21.57
L (obs.)	100.34	94.07	85.74	76.83	65.79	50.56	34.87	20.99

n-Propyl formate, C₄H₈O₂. $v_0=71.22$. $\frac{db}{dt}=0.07281$.

θ	70	100	130	160	190	220	250	260
L (calc.)	90.57	83.10	75.74	67.64	58.87	47.64	30.95	20.79
L (obs.)	89.05	82.66	75.96	68.29	60.28	49.62	31.99	21.02

Ethyl acetate, C₄H₈O₂. $v_0=70.98$. $\frac{db}{dt}=0.07593$.

θ	70	100	130	160	190	220	230	240
L (calc.)	89.38	81.43	73.21	64.17	54.01	40.73	34.69	26.62
L (obs.)	87.42	82.15	74.69	65.91	56.40	42.63	36.05	27.17

Methyl propionate, C₄H₈O₂. $v_0=70.36$. $\frac{db}{dt}=0.07326$.

θ	70	100	130	160	190	220	240	250
L (calc.)	91.09	83.03	74.99	66.34	56.66	44.71	33.01	23.92
L (obs.)	88.94	82.75	76.04	68.15	58.95	47.14	34.41	24.30

n-Propyl acetate, C₅H₁₀O₂. $v_0=85.61$. $\frac{db}{dt}=0.08716$.

θ	90	120	150	180	210	240	260	270
L (calc.)	84.07	75.93	68.07	60.02	51.07	39.67	28.91	20.15
L (obs.)	81.65	76.33	69.79	62.80	54.29	42.40	30.70	20.57

TABLE II. (*continued*).*Non-associated Liquids.*

Ethyl propionate, $C_5H_{10}O_2$. $v_0 = 84.41$. $\frac{db}{dt} = 0.08859$.

θ	90	120	150	180	210	240	260	270
L (calc.)	81.46	73.96	66.19	58.16	49.25	37.58	26.05	15.16
L (obs.)	80.49	75.17	67.69	59.94	51.82	40.23	27.84	15.65

Methyl butyrate, $C_5H_{10}O_2$. $v_0 = 84.85$. $\frac{db}{dt} = 0.08459$.

θ	100	130	160	200	230	260	270	280
L (calc.)	80.79	73.28	65.88	55.20	45.26	32.00	25.26	11.77
L (obs.)	77.80	72.37	66.53	57.41	48.08	34.44	26.96	11.16

Methyl isobutyrate, $C_5H_{10}O_2$. $v_0 = 84.59$. $\frac{db}{dt} = 0.08643$.

θ	90	120	150	180	210	240	250	260
L (calc.)	77.16	70.24	63.17	55.29	46.49	34.10	28.64	21.01
L (obs.)	76.32	70.65	64.51	57.19	48.89	36.06	30.17	21.91

The foregoing table shows that for non-associated substances the theory advanced by the authors is in close accordance with the observed energy changes, the calculated latent heats seldom varying by more than 2 or 3 units from the values obtained by Young. In the case of the characteristically "normal" substances, pentane, benzene, fluorobenzene, and carbon tetrachloride, the agreement is still more satisfactory, the divergences hardly ever amounting to 1 unit.

With regard to the remaining substances considered in table II, it may be noted that the differences between calculated and observed latent heats show in many cases a systematic variation with temperature. For example, the calculated values for most of the esters are rather too high at low temperatures and too low at high temperatures, whilst for ethyl ether the agreement which is satisfactory at higher temperatures becomes less so as the temperature falls. Discrepancies of this kind may probably be ascribed to slight inaccuracies in the extrapolation of the rectilinear diameter to the absolute zero, in Mills' relation, or in the assumption that $\frac{db}{dt}$ is constant.

The numbers for the halogen derivatives of benzene are also worthy of note, as, with the exception of those for fluorobenzene, the calculated values are all much too high, the mean percentage differences between the calculated and the observed latent heats of

benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene being respectively 0.57, 0.92, 3.22, 5.54, and 5.32. These results seem to indicate the occurrence of a certain amount of molecular association in chloro-, bromo-, and iodo-benzene in the liquid state.

For substances which are considerably associated in the liquid state, many of the regularities observed with normal liquids are no longer valid. Mills' relation, $\left(\frac{\delta p}{\delta t}\right)_c = \frac{2R}{v_c}$, which was used in the foregoing calculations, is not true for substances with which the association persists up to the critical temperature. The influence of changing association also affects in a marked manner the variation of b with temperature, and in all probability $\frac{db}{dt}$ is a variable and complex function. In addition, the great curvature of the diameter makes the extrapolation to the volume at absolute zero very uncertain. In view of these facts, it is not surprising that, as table III shows, the latent heats calculated by this method diverge widely from those determined by Young's pressure measurements. Although the deductions of this paper give no means of measuring molecular association, it seems clear that the lack of agreement obtained constitutes a very sensitive method of indicating such a condition.

TABLE III.

Associated Substances.

θ .	Methyl alcohol.		Ethyl alcohol.		Propyl alcohol.		Acetic acid.	
	L (calc.).	L (obs.).	L (calc.).	L (obs.).	L (calc.).	L (obs.).	L (calc.).	L (obs.).
0	259.93	289.17	—	220.9	—	—	—	—
50	252.03	274.14	312.37	216.0	—	—	181.67	88.14
100	231.75	246.01	185.02	197.1	196.69	164.0	157.10	92.32
150	195.56	206.13	133.74	164.7	132.93	135.3	135.76	90.74
200	168.23	151.84	92.41	116.6	92.39	102.2	115.81	85.55
250	—	—	—	—	47.13	50.6	91.64	75.55
300	—	—	—	—	—	—	56.44	48.97

On comparing the values of v_0 , b_k and $\frac{db}{dt}$ for the normal substances considered in tables I and II, a remarkable regularity makes itself apparent. As will be seen from the last column of table IV, the value of $\frac{1}{v_0} \frac{db}{dt}$ is almost a constant; that is, the effect of rise of temperature on the true molecular volume of all normal substances is the same, and amounts to an increase of the van der Waals constant b by about 0.1 per cent. for a rise of temperature of 1° .

TABLE IV.

Substance.	$v_0 = b_0$.	b_c .	$\frac{db}{dt}$.	$\frac{1}{v_0} \frac{db}{dt} \times 10^5$.
{ <i>n</i> -Pentane	80.27	120.30	0.0892	111
{ β -Methylbutane	79.95	120.52	0.08804	110
{ <i>n</i> -Hexane	93.58	143.14	0.09760	104
{ β -Dimethylbutane	92.69	139.83	0.09241	100
{ <i>n</i> -Heptane	108.79	166.56	0.10701	98
{ <i>n</i> -Octane	123.85	190.63	0.11732	95
{ β -Dimethylhexane	123.29	188.10	0.11788	96
<i>cyclo</i> Hexane	79.00	120.07	0.07427	94
Benzene	65.19	99.81	0.06166	95
Fluorobenzene	69.63	105.85	0.06472	93
Chlorobenzene	79.69	120.46	0.06449	81
Bromobenzene	83.71	126.54	0.06392	76
Iodobenzene	90.05	136.94	0.06503	72
Carbon tetrachloride	70.43	107.54	0.06674	95
Stannic chloride	87.28	136.03	0.08239	94
Ethyl ether	72.37	110.14	0.08091	112
Methyl formate	43.59	66.93	0.04793	110
{ Ethyl formate	57.89	89.06	0.05922	102
{ Methyl acetate	57.82	88.63	0.06080	105
{ Propyl formate	71.22	110.38	0.07281	102
{ Ethyl acetate	70.98	110.70	0.07593	107
{ Methyl propionate	70.36	109.22	0.07326	104
{ Propyl acetate	85.61	133.48	0.08716	102
{ Ethyl propionate	84.41	132.77	0.08859	105
{ Methyl butyrate	84.85	131.74	0.08459	100
{ Methyl isobutyrate	84.59	131.31	0.08643	102

The halogen derivatives of benzene again show an anomalous behaviour, giving much smaller values of $\frac{1}{v_0} \frac{db}{dt}$ than any of the other substances investigated, a further indication that these substances are not wholly unassociated.

Summary.

(1) A method has been described by which the latent heats of vapours can be calculated from the volume relations of the substances in the liquid and gaseous states.

(2) The latent heats of non-associated substances calculated in the manner described agree satisfactorily with the values of Young.

(3) The values of the van der Waals constant b , and its variation with temperature, have been found for twenty-six normal substances, and it has been shown that for non-associated substances

$\frac{1}{v_0} \frac{db}{dt}$ is approximately constant.

(4) The halogen derivatives of benzene show anomalies which can be explained by the assumption that they are associated to a certain extent.

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