LIX. *The van der Waals Formula (and the Latent Heat of Vaporization)*. By T. CARLTON SUTTON, B.Sc., *Government Research Scholar in the University of Melbourne**.

IN the *Journal of the Chemical Society*, 1914 (p. 734), Applebey and Chapman derive a "formula for the latent heat of vaporization" which gives results in good agreement with those of Mills and Young†.

The impression given by their paper is that the Mills-Young values are "observed," and may be used as experimental data confirming theoretical results. This is so, only in the sense that the Mills-Young values are "calculated from observed" values of pressure, temperature, and volume by a process very similar to that which Applebey and Chapman themselves employ (see Appendix).

This considerably modifies the inferences that should be drawn from their work.

The chief difference in the processes is that Mills‡ uses the Biot's formula

$$\log p = A + B\alpha^t + C\beta^t$$

to express the relation between vapour-pressure and temperature, where A B C α β are five arbitrary constants chosen to suit the measured values of the vapour-pressure, t is the temperature, and p the saturation vapour-pressure; whereas Applebey and Chapman prefer to use a form of van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v-b) = Rt,$$

in which b is to be treated as a variable. They find afterwards that b varies uniformly with the temperature. Consequently, the equation may be put in the form

$$\left(p + \frac{a}{v^2}\right)(v-b_c - \gamma \overline{t_c - t}) = Rt,$$

where t_c is the critical temperature, $\gamma = \frac{db}{dt} = \text{constant}$, and b_c is the value of b at the critical temperature.

* Communicated by Prof. Sydney Young.

† *Sci. Proc. R. Dublin Soc.* 1910, p. 412.

‡ *Journal of Physical Chemistry*, 1902, 1905 *et seq.*

As shown in the Appendix, this leads to the results

$$L = t(v_2 - v_1) \{ B \log \alpha \cdot \alpha^t + C \log \beta \cdot \beta^t \}$$

and

$$L = R t \log \frac{v_2 - b}{v_1 - b} + R t^2 \left(\frac{1}{v_1 - b} - \frac{1}{v_2 - b} \right) \frac{db}{dt} \quad (B)$$

respectively, where L , v_1 and v_2 are the molecular latent heat, molecular volume of liquid and molecular volume of vapour at temperature t , b is the van der Waals' constant closely connected with the volume actually occupied by the molecule, and R is the gas constant.

The following table compares the results so calculated with such experimental measurements as have been actually made. The latter are meagre, and have been made at the boiling-points (under one atmosphere pressure) only.

	Temp.	L (per grm.) Calculated.		L Obsd.	Date, &c.
		Mills-Young.	Applebey & Chapman.		
Ethyl Ether	34°·5 C.	84·13	87·3	88·4	Wirtz, 1890.
Hexane	68°·0	79·51	79·5	79·4	Mabery and Goldstein, 1902.
Heptane	98°	76·2	76·1	74·0	M. & G., 1902.
Octane	124°·9	70·75	68·4	70·92	Longuinine, 1895.
	125°	70·74	68·4	71·1	M. & G., 1902.
Hexamethylene ...	70°	88·5	86·0	87·3	M. & G., 1902.
Benzene.....	80°·1	95·43	94·8	92·91	Wirtz, 1890.
	80°·35	95·39	94·8	93·45	Schiff, 1886.
Stannic Chloride ...	112°·5	31·0	30·6	30·53	Andrews, 1848.
Methyl Formate ...	32°·9	113·4	118·8	115·2	Berthelot and Ogier, 1881.
	32°·5	113·52	118·9	110·45	Brown, 1903.
Ethyl Formate	54°·2	97·04	95·8	100·4	B. & O., 1881.
	54°·2	97·04	95·8	100·1	Brown, 1903.
	53°·5	97·18	96·0	92·15	Schiff, 1886.
Propyl Formate ...	81°·2	87·19	88·4	85·25	Schiff, 1886.
	81°·2	87·19	88·4	90·36	Brown, 1903.
Methyl Acetate.....	57°·3	99·06	105·3	93·95	Schiff, 1886.
	57°·3	99·06	105·3	98·26	Brown, 1903."
Ethyl Acetate	73°·1	86·88	88·6	84·28	Wirtz, 1890.
	74°·0	86·76	88·5	105·0	Schall, 1884.
	77°·0	86·27	88·0	83·1	Schiff, 1886.
	77°·3	86·22	88·0	88·37	Brown, 1903.
Propyl Acetate.....	102°·3	79·44	80·7	77·3	Schiff, 1886.
	102°·3	79·44	80·7	80·45	Brown, 1903.
Methyl Propionate..	80°·0	87·07	88·6	84·15	Schiff, 1886.
	78°·95	87·26	88·8	89·0	Brown, 1903.
Ethyl Propionate...	98°·7	79·4	79·8	77·1	Schiff, 1886.
	99°·2	79·33	79·7	80·3	Brown, 1903.
Methyl Butyrate ...	93°	79·0	81·6	86·0	Schall, 1884.
	102°·3	77·40	80·0	77·25	Schiff, 1886.
	102°·5	77·36	80·0	79·75	Brown, 1903.
Methyl Isobutyrate.	92°·5	75·93	75·6	75·5	Schiff, 1886.
	92°·4	75·95	75·6	79·0	Brown, 1903.

The modified van der Waals' formula

$$\left(p + \frac{a}{v^2}\right)(v - b - \gamma \delta t) = Rt,$$

$$\text{where} \quad \gamma = \frac{db}{dt} = \text{constant},$$

leads to results very close to the measured results. In many ways it is to be preferred to the Biot's formula

$$\log p = A + B\alpha' + C\beta^t.$$

(1) It contains three adjustable constants, whereas Biot's formula contains five.

(2) Each of these three constants has a physical significance.

(3) The agreement with the measured values of p , v and t is very close—the discrepancies being of the same order of magnitude as when Biot's formula is used.

(4) The derived equation (B) gives values of the latent heat of vaporization in satisfactory agreement with the measured values (*e. g.* at the boiling-point under one atmosphere pressure—see Table), whereas Bakker, using the unmodified van der Waals' equation, obtained results 20 per cent. too low*.

(5) The tables in Applebey and Chapman's paper (pp. 739–742) show that the agreement between the two series of calculated latent heats is still better at higher temperatures.

The fact that $\frac{db}{dt}$ is found to be constant, suggests that the molecule expands uniformly with increase of temperature.

[A uniformly expanding atom has been assumed by Schott in the Adams' Prize Essay for 1908†, and by Richards in some researches published in the *Zeits. Phys. Chem.* xlii. and subsequent vols.]

Applebey and Chapman remark (p. 742–3) “for halogen derivatives” of benzene “the calculated values are all much too high, the mean percentage differences for chlorobenzene, bromobenzene, and iodobenzene being respectively 3.22, 5.54, 5.32.” There are no experimental results with which to compare these two series of calculated values. It seemed desirable, therefore, to obtain Mill's constant‡, μ' , for each of these substances.

* Bakker, *Zeits. Phys. Chem.* 1895, p. 519.

† Electromagnetic Radiation (Schott), Camb. Univ. Press, 1912.

‡ See ‘Journal of Physical Chemistry,’ 1905 and 1909.

Temperature.	MILL'S CONSTANT.		
	Calculated by Biot's formula.		Calculated by Applebey's formula.
	Calc. 1905.	Recalc. from revised data 1909.	
130° C.	79.46	79.9	85.9
160°	80.83	80.9	85.6
190°	81.34	81.5	84.5
220°	81.84	82.2	83.9
240°	83.06	82.8	84.0
270°	84.93	82.5	85.4

<i>Bromobenzene.</i>			
100° C.	56.93	...	59.8
150°	54.10	54.6	59.6
180°	54.98	55.0	59.6
210°	55.9	55.7	59.2
230°	56.25	56.0	58.7
250°	56.44	55.8	58.8
260°	56.92	56.1	58.7
270°	57.15	56.2	58.6

<i>Iodobenzene.</i>			
190° C.	41.87	42.9	45.9
220°	43.64	43.5	46.0
250°	44.38	43.6	46.5
270°	45.10	43.2	46.9

Mills has twice calculated the values of μ' , employing Biot's formula to represent the connexion between saturation-pressure and temperature. The calculations of 1905 show irregularities in the values obtained in these same cases, chlorobenzene, bromobenzene, and iodobenzene. The recalculations of 1909, based on Young's revised data, show irregularities that are smaller, but are still much greater than those given by other substances. When the modified van der Waals' equation is used, these irregularities still occur. It will be seen that they are smaller than in the previous cases, though only slightly so. What seems more important is the fact that, in general, maximum values obtained by means of Biot's formula correspond to minimum values obtained by the van der Waals' relation, and so on. This suggests that the error is due to some change in the liquids not accounted for by either of the formulæ.

It seems therefore that in the case of these non-associated

liquids, the differences between the two series of calculated values of latent heat are quite as likely to be due to a divergence of Biot's formula from the facts as to such a divergence of the modified van der Waals' relation.

Consequently it will be seen that this modified van der Waals' relation, and the derived expression (B) for the latent heat of vaporization, hold good for *all* the non-associated liquids examined and for *none* of the associated liquids; hence the agreement between the two series of calculated latent heats, and the variations in the value of Mills' constant (see above) give delicate tests of association in a liquid.

My thanks are due to Professor Young for supplying some data I had overlooked, and for kindly offering to read the proofs of this paper.

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APPENDIX.

In the following it is shown in detail that the methods of calculation used by Mills-Young and by Applebey-Chapman are essentially the same.

The data employed in the Mills-Young and the Applebey-Chapman calculations are the measurements of the vapour-pressure and the vapour-density of thirty-two pure liquids made by or under the direction of Dr. Sydney Young. These have been collected and revised, and are published in the Scientific Proceedings of the Royal Dublin Society, 1910, pp. 412-443. With them appear Dr. Mills' series of calculated latent heats that we are about to discuss.

In each case the process of reduction has consisted of—

- (1) Finding some formula connecting the temperature with either the vapour-pressure or the specific volume of the saturated vapour. Determining the constants of this formula over a range extending to the critical temperature.
- (2) Differentiating this formula and substituting the value of $\frac{dp}{dt}$ so found in the Clausius-Clapeyron relation

$$L = t(v_2 - v_1) \frac{dp}{dt},$$

where v_2 and v_1 are the molecular volume of vapour and liquid respectively, t the absolute temperature, p the saturation-pressure, and L the molecular latent heat of vaporization.

(1) For the vapour-pressure formula, Mills* has chosen Biot's form

$$\log p = A + B\alpha^t + C\beta^t, \quad . \quad . \quad . \quad (a)$$

involving five arbitrary constants.

Applebey and Chapman prefer to use a form such as van der Waals' equation (J. C. S. 1914, p. 734),

$$\left(p + \frac{a}{v^2}\right)(v-b) = Rt,$$

but treat b as a variable (p. 735). Later (p. 736) they find that $\frac{db}{dt}$ is a constant, and is to be chosen to suit the data (see method p. 737).

This is equivalent to employing the three-constant formula

$$\left(p + \frac{a}{v^2}\right)\left(v-b - \frac{db}{dt} \delta t\right) = Rt, \quad . \quad . \quad . \quad (b)$$

where a , b , and $\frac{db}{dt}$ are adjustable constants and R is the gas constant, b is the value of the van der Waals' constant at the critical temperature, and δt the difference between the critical temperature and the absolute temperature considered.

The constants of the formulæ (a) and (b) are chosen so as to suit the same series of measurements—that is to say, so that their graphs may agree as closely as possible with the experimental graph. They are, therefore, the same relation expressed in different forms.

(2) By differentiating to obtain $\frac{dp}{dt}$, and substituting its value in the Clausius-Clapeyron relation, Mills gets

$$L = t(v_2 - v_1) \{ B \log \alpha \cdot \alpha^t + C \log \beta \cdot \beta^t \},$$

while Applebey and Chapman by an ingenious but mathematically similar process (pp. 735-6) obtain

$$L = Rt \log \left(\frac{v_2 - b}{v_1 - b} \right) + Rt^2 \left(\frac{1}{v_1 - b} - \frac{1}{v_2 - b} \right) \frac{db}{dt}.$$

These two formulæ are derived from relations which approximately represent the same experimental results, by means of the same mathematical processes; and should, therefore (if the approximation is good), give concordant values of L .

* Journal of Physical Chemistry, 1902, 1904, &c.