LIII. Latent heats of vaporization and expansion

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2 lamberts. Doubtless some function of the intensity and the angle could be devised such that, in a corresponding sense, one candle-power per square centimetre would be equal to π lamberts, but we cannot discover a function which has the least intrinsic plausibility. Doubtless the American committee have succeeded where we have failed, but they have been unduly modest in concealing their ingenuity; they may fairly be asked to explain how they have arrived at their surprising result and why they have preferred it to the simple and obvious convention which gives the result that 1 candle-power per square centimetre equals 1 lambert.

May 27, 1922.

LIII. *Latent Heats of Vaporization and Expansion.*

By D. L. HAMMICK*.

ACCORDING to van der Waals, the pressure in a homogeneous fluid system is $p + \frac{a}{v^2}$. When the system expands, work is done against the pressure. The value of this work for the expansion of 1 gram of a liquid (volume v_1 c.c.) until its volume is v_2 c.c., the specific volume of the liquid when completely vaporized, is given by

$$\begin{aligned} A &= \int_{v_1}^{v_2} \left(p + \frac{a}{v^2} \right) dv \\ &= \int_{v_1}^{v_2} p dv + \int_{v_1}^{v_2} \frac{a}{v^2} dv \\ &= pv_1 - pv_2 - \frac{a}{v_1} + \frac{a}{v_2}. \end{aligned}$$

When v_2 is large when compared with v_1 , this expression becomes

$$A = -pv_2 - \frac{a}{v_1},$$

or, putting pv_2 equal approximately to $\frac{RT}{M}$,

$$A = -\frac{RT}{M} - \frac{a}{v_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* Communicated by the Author.

From (1) we have, at constant volume,

$$\begin{aligned} T \left(\frac{dA}{dT} \right)_v &= -\frac{RT}{M} - \frac{1}{v_1} \cdot \frac{da}{dT} \cdot T \\ &= -\frac{RT}{M} - \frac{a}{v_1} \bar{a}T \\ &\left(\bar{a} = \frac{1}{a} \frac{da}{dT} \right). \end{aligned}$$

Hence, substituting in the equation

$$\begin{aligned} A - U &= T \left(\frac{dA}{dT} \right)_v, \\ -U &= -A + T \frac{dA}{dT} = \frac{a}{v_1} (1 - \bar{a}T) \quad . \quad . \quad . \quad (2) \\ &= \lambda_{\text{ex}}, \text{ the latent heat of the expansion.} \end{aligned}$$

Now Davies (Phil. Mag. [6] xxiv. p. 421) has obtained the following expression for π , the initial pressure in a fluid:—

$$\begin{aligned} \pi &= \frac{4R}{v_c} (2T_c - T) \\ (v_c \text{ and } T_c \text{ are critical volume and temperature}). \end{aligned}$$

Hence
$$\frac{1}{\pi} \left(\frac{d\pi}{dT} \right)_v = - \frac{1}{2T_c - T}.$$

Davies has also shown (Phil. Mag. [6] xxiii. p. 415) that $\frac{1}{2T_c - T} = \alpha$, the coefficient of cubical expansion, so that

$$\frac{1}{\pi} \left(\frac{d\pi}{dT} \right)_v = -\alpha. \quad . \quad . \quad . \quad (3)$$

But, if $\pi = \frac{a}{v^2}$, we get from (3) :

$$\frac{1}{a} \left(\frac{da}{dT} \right)_v = -\alpha.$$

Substituting in (2)

$$\lambda_{\text{ex}} = \frac{a}{v} (1 + \alpha T). \quad . \quad . \quad . \quad (4)$$

When $T=0$, we find $\lambda_{\text{ex}} = \frac{a}{v_0}$; in other words, at the absolute zero the expression becomes identical with Bakker's expression for the latent heat of vaporization.

The question now arises as to the connexion between the value for the latent heat of expansion as given by (4) and the latent heat of vaporization at ordinary temperatures. The two latent heats would be equal, provided that no change in the internal energy of the substance occurred during the transition, at constant volume, from the liquid to the vapour phase. In other words, the condition for equality is :

$$\int_0^T C_v dT - \int_0^T c_v dT = 0. \quad . \quad . \quad . \quad (5)$$

(C_v , c are the specific heats at constant volume respectively.)

If (5) does not hold, then the difference between the latent heat of vaporization and λ_{ex} . of equation (4) will be

$$\int_0^T (C_v - c_v) dT = H.$$

Again, if during the passage from the liquid to the gaseous state a change in molecular aggregation occurs, a further quantity of heat, h , representing heat of association, must be taken into consideration. Hence we may put

$$\lambda_{vap.} = \lambda_{ex.} + H + h. \quad . \quad . \quad . \quad (6)$$

In the Table values of $\lambda_{ex.}$, calculated according to equation (4) at the boiling-point, are compared with the observed values of $\lambda_{vap.}$, the latent heat of vaporization. Values of " a " are given as atmospheres pressure $\div$ (volume of 1 gramme molecule of gas at N.T.P.)² (Guye and Frederich, *Arch. Sci. phys. et natur. Genève*, ix. p. 22, 1900). Specific volumes and α , the coefficients of expansion, are taken from Young (*Sci. Proc. Roy. Dubl. Soc.* xii. p. 414, 1910) and Tyrer (*Trans. Chem. Soc.* 1914, p. 2534). The latent heats of vaporization refer to 1 gramme of liquid, and are mainly Young's values (*loc. cit.*).

It will be seen from the Table that the values of $\lambda_{ex.}$ at the boiling-point agree very well with the values of the latent heat of vaporization. At the boiling-point, therefore, we have, in equation (6),

$$H + h = 0.$$

For "normal" or unassociated liquids $h=0$, and hence

$$H = \int_0^T (C_v - c_v) dT = 0.$$

TABLE.

Substance.	T _{b.p.} ° A.	a. ats. (22·4 litres) ²	v. c.c. per gram.	$\frac{a}{v}$ cals. per gram.	a.	1 + aT.	$\lambda_{ex.}$ calc. cals. per gr.	$\lambda_{vap.}$ observed. cals. per gr.
Hydrogen	20·3	·00042 ²	1·429 ¹	89·47	·0·1116 ¹	1·227	110	{ 108·5- 113·2 ²
Nitrogen	67	·00276 ²	1·230 ⁴	34·82	·0·569 ⁴	1·438	50·04	49·83
Oxygen	85	·00272	·857 ⁴	37·75	·0·426 ⁴	1·362	51·4	53·8
Argon	87	·00260	·712 ⁴	27·95	·0·385 ⁴	1·385	38·7	37·5 ⁵
Ammonia	238	·0·798 ²	1·476 ⁶	227·7	·0·176	1·419	323	321·
N ₂ O	253	·0750	1·00	47·15	·0·186	1·472	69·4	66·9
Ether	308	·03688	1·431	56·08	·0·169	1·52	85·2	84·0
n-pentane	313	·03915	1·622	59·96	·0·163	1·511	90·6	84·3
Methyl formate ...	313	·02355	1·059	75·22	·0·157	1·491	112·1	110·6
OS ₂	323	·02412	·822	61·8	·0·126	1·407	86·95	85·0
Ethyl formate ...	323	·03302	1·133	64·64	·0·159	1·513	97·8	97·9
Methyl acetate ...	333	·03316	1·136	61·88	·0·158	1·528	94·6	98·6
Ethyl acetate ...	343	·04383	1·20	57·39	·0·152	1·521	87·3	85·8
n-hexane	343	·05383	1·633	54·12	·0·159	1·544	83·6	81·9 ¹⁰
Fluor-benzene.....	353	·04272	1·053	53·61	·0·142	1·503	80·6	80·1
Propyl formate ...	353	·04388	1·199	57·46	·0·150	1·530	87·9	87·5
Methyl propionate	353	·04330	1·189	57·17	·0·166	1·586	90·7	89·0 ⁸
COCl ₂	353	·04148	·676	31·6	·0·135	1·470	46·7	46·0
Benzene	353	·03945 (M).	1·233	64·03	·0·138	1·487	95·2	95·4
n-heptane	373	·06876	1·633	51·26	·0·156	1·582	81·1	75·8
Propyl acetate ...	373	·05659	1·257	52·67	·0·155	1·578	83·1	80·5 ⁹
Ethyl propionate..	373	·05582	1·258	51·9	·0·159	1·593	82·7	81·8 ⁸
Methyl butyrate...	373	·05577	1·240	52·55	·0·156	1·581	83·1	79·7 ⁸
Methyl isobutyrate	363	·05339	1·239	50·3	·0·155	1·565	78·7	76·3
Toluene	383	·05240	1·283	58·75	·0·125	1·478	86·8	86·8 ⁸
SnCl ₄	383	·05926	·5021	21·12	·0·141	1·542	32·6	31·6
n-octane	393	·08351	1·621	48·2	·0·154	1·606	77·4	77·4
Chlor-benzene.....	404	·05580	·983	47·54	·0·124	1·506	71·6	74·2
Bromo-benzene ...	433	·05692	·769	36·5	·0·113	1·490	54·4	55·2
Iodo-benzene	453	·06592	·633	30·5	·0·114	1·516	46·3	46·7
Acetic acid... ..	393	·03732	1·068	118·2	·0·123	1·484	176·0	94·4
Water	373	·0118	1·044	424·7	·0·766	1·286	546	539
Acetone	329	·02617	1·321	71·56	·0·149	1·492	106·8	125·3
Ethyl alcohol	353	·02512	1·360	106·3	·0·125	1·441	153	220·9
Methyl alcohol ...	333	·01959	1·324	176·0	·0·121	1·402	246·6	289·2

¹ Dewar.² Kaye and Laby's Tables.³ Keesom and Onnes (1913).⁴ Baly and Donnan, Jour. Chem. Soc. lxxxi. p. 907 (1902).⁵ Eucken, *Ber. deut. phys. Gesellsch.* xviii. p. 4 (1916).⁶ Lunge.⁷ Estreicher.⁸ Marshal and Ramsay, Phil. Mag. (5) xli. p. 28 (1896).⁹ Brown, Jour. Chem. Soc. lxxxiii. p. 987 (1903), lxxxvii. p. 265 (1905).¹⁰ Tyrer.

At the end of the Table are given some results for liquids ordinarily regarded as associated. It will be noticed that in the case of water the value of $H + h$ is approximately zero; in other words, $h + H$ must be nearly equal but opposite in sign.

Agreement between the values of λ_{ex} and λ_{vap} is not found at temperatures other than the boiling-point. Thus for ether at 0°C , $\lambda_{\text{ex}} = 85.5$ cal.; $\lambda_{\text{vap}} = 92.5$ cal. And from equation (4) it is easy to show that the slope of the λ_{ex} curve is given by

$$\frac{1}{\lambda_{\text{ex}}} \frac{d\lambda_{\text{ex}}}{dT} = -\frac{\alpha^2 T}{1 + dT}.$$

Now at the boiling-point, αT is approximately .5 (*vide* Table above). Hence

$$\frac{1}{\lambda_{\text{ex}}} \frac{d\lambda_{\text{ex}}}{dT} = -.33\alpha.$$

The average value of $\frac{1}{\lambda_v} \cdot \frac{d\lambda_{\text{vap}}}{dT}$ in the neighbourhood of the boiling-point is $2\alpha - 3\alpha$.

The Dyson Perrins Laboratory, Oxford.
May 12th, 1922.

LIV. *On the Faraday-Tube Theory of Electro-Magnetism.*
By the late WILLIAM GORDON BROWN.*

1. **T**HE method of describing a field of force by means of lines or tubes of induction, which originated with Faraday, was given a quantitative form by Sir J. J. Thomson †, and further discussed by N. Campbell in his book 'Modern Electrical Theory.' Since Maxwell himself looked on his work as a mathematical theory of Faraday's lines of force, one is tempted to examine the original physical theory for hints

* Communicated by Dr. C. G. Knott, F.R.S., General Secretary, R.S.E.

The young author had just finished his school life at George Watson's College, Edinburgh, when the outbreak of war in 1914 called him to the service of King and Country. He met his death in France on November 13, 1916, at the age of 21. The paper was put in final form about a year earlier when W. G. Brown, after serving in Gallipoli, was in hospital. A short sketch of his life and of his other mathematical notes will be found in the Proceedings of the Roy. Soc. Edin. vol. xlii. 1921.

† 'Recent Researches,' chap. i.; 'Electricity and Matter,' chap. i.