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VII. *The Determination of a Constant in Capillarity.* By
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WHEN the area of the surface of a liquid is increased the increase in the amount of energy in the surface-film of the liquid is equal to the sum of the external work done and the amount of heat absorbed from the surrounding bodies to keep the temperature constant during the process. The relation between these quantities can be immediately obtained by means of Helmholtz's free energy equation connecting the total energy with the free energy, which gives

$$E + T \frac{d\lambda}{dT} = \lambda, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where λ denotes the surface-tension and E the total energy corresponding to the temperature T . λ is equal to the external work done, and $-T \frac{d\lambda}{dT}$ is therefore equal to the amount of heat absorbed from the surrounding bodies. This formula was first given by Lord Kelvin.

Whittaker† has calculated the values of E , the total energy for different temperatures, for a number of liquids, using the surface-tension determinations of Ramsay and Shields‡. He found that the energy E per cm^2 of the film of a liquid is proportional to the product of the internal latent heat of evaporation into the absolute temperature of the liquid, or

$$E = KTL, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where L is the internal latent heat of evaporation corresponding to the temperature T , and K is a constant. The constant K was found to be different for the various liquids. The extent of the agreement of this empirical law with the experimental facts is shown by the following tables taken from Whittaker's paper.

* Communicated by the Author.

† Proc. Roy. Soc. A. vol. lxxxi. p. 21 (1908).

‡ Phil. Trans. A. vol. clxxxiv. p. 647 (1893).

Ether.

T.	E.	L.	$\frac{E \times 10^4}{\text{TL or } K10^4}$
313	49.1	75.36	20.8
323	48.9	73.01	20.8
333	48.9	70.79	20.5
343	47.8	68.35	20.4
353	47.1	65.85	20.3
363	46.1	63.31	20.1
373	45.5	60.33	20.2
383	44.7	58.07	20.1
393	43.8	54.91	20.3
403	42.6	51.62	20.5
413	41.1	48.31	20.6
423	39.3	44.38	20.9

Methyl formate.

T.	E.	L.	$\frac{E \times 10^4}{\text{TL or } K10^4}$
303	69.4	107.49	21.3
313	68.8	103.95	21.1
323	68.2	99.51	21.2
333	67.5	95.59	21.2
343	67.3	92.16	21.3
353	66.2	88.03	21.3
363	65.5	85.10	21.2
373	64.6	82.43	21.0
383	63.8	79.21	21.0
393	62.9	75.92	21.1
403	61.8	71.95	21.3
413	60.4	68.10	21.5
423	58.8	64.03	21.7

Benzene.

T.	E.	L.	$\frac{E \times 10^4}{\text{LT or } K10^4}$
353	59.5	85.6	19.7
363	60.2	83.7	19.8
373	60.9	82.0	19.9
383	61.1	80.0	20.0
393	60.7	78.1	19.8
403	60.1	76.1	19.6
413	59.4	74.1	19.4
423	58.8	71.9	19.3
433	58.0	69.7	19.2
443	57.2	67.5	19.1
453	56.1	65.1	19.0
463	55.0	62.7	19.0
473	54.0	59.9	19.1
483	52.9	57.0	19.3
493	51.5	53.8	19.4
503	49.9	50.5	19.7
513	48.1	46.6	19.1

Carbon tetrachloride.

T.	E.	L.	$\frac{E \times 10^4}{\text{LT or } K10^4}$
363	57.9	40.62	39.3
373	57.5	39.68	38.9
383	56.8	38.64	38.4
393	56.4	37.63	38.2
403	55.6	36.58	37.7
413	54.8	35.56	37.3
423	53.9	34.42	37.0
433	53.1	33.28	37.9
443	52.6	32.07	37.0
453	52.2	30.83	37.4
463	51.7	29.52	37.8
473	50.8	28.22	37.1
483	50.3	26.83	37.8
493	49.8	25.35	37.8
503	47.3	23.73	37.6

The object of this paper is to find a value for K of a liquid in terms of its absolute constants. Such a determination is evidently desirable.

Ramsay, following Eötvös, has shown that the surface-tension of a liquid at the absolute temperature T is connected with the absolute temperature and other quantities by

Chloro-benzene.

T.	E.	L.	$\frac{E \times 10}{TL}$ or K10 ⁴ .
423	59.8	65.81	21.4
433	59.9	64.12	21.6
443	60.0	63.02	21.5
453	60.0	61.46	21.5
463	59.3	59.97	21.3
473	58.6	58.31	21.3
483	58.1	56.81	21.2
493	57.4	55.29	21.1
503	56.7	53.83	20.9
513	55.9	52.43	20.8
523	55.1	50.81	20.7
533	53.8	49.09	20.6

the equation

$$\lambda v^{2/3} = A(T_c - T - a), \quad (3)$$

where v denotes the molecular volume of the liquid, and A is a constant which is practically the same for all liquids, being equal to about 2.1, T_c is the critical temperature, and a is another constant which is also approximately the same for all liquids, its mean value being about 5. Substituting for λ in equation (1) by means of equation (3), we obtain

$$E = A \frac{(T_c - T - a)}{v^{2/3}} + \frac{AT}{v^{2/3}} + \frac{2}{3} TA \frac{(T_c - T - a)}{v^{5/3}} \frac{dv}{dT}.$$

Let us suppose that λ refers to a temperature much below the critical temperature of the liquid, say near the absolute zero. The value of $\frac{dv}{dT}$ is then a very small fraction, and $T(T_c - T - a)$ small in comparison with $(T_c - T - a)$. The third term on the right-hand side of the last equation may at low temperatures be, therefore, neglected in comparison with the other terms, and in that case

$$E = \frac{A}{v^{2/3}} (T_c - a).$$

The molecular volume is given by $v = \frac{m}{\rho}$, where m is the molecular weight and ρ the density of the liquid. Substituting for v in the last equation we have

$$E = \frac{\rho^{2/3} A (T_c - a)}{m^{2/3}}.$$

And since $E = KLT$, we have

$$K = \frac{\rho^{2/3} A}{m^{2/3} L T} (T_c - a). \quad . \quad . \quad . \quad . \quad (4)$$

The latent heat of evaporation L_1 of a liquid is given by the well-known thermodynamical relation

$$L_1 = (v_1 - v_2) T \frac{dp}{dT},$$

where v_1 and v_2 denote respectively the volumes of a gram of the saturated vapour and the liquid, and p denotes the pressure. For temperatures well removed from the critical temperature the vapour behaves approximately as a perfect gas, and this equation may then be written

$$L_1 = \frac{RT^2}{mp} \frac{dp}{dT},$$

where R denotes the gas constant. If the equation be written in the form

$$\frac{L_1 m}{T} = \frac{RT}{p} \frac{dp}{dT},$$

and the temperatures and pressures at the right-hand side be expressed in terms of the critical temperature and pressure, we obtain

$$\frac{L_1 m}{T} = \frac{R \alpha T_c}{\beta p_c} \frac{p_c}{T_c} \frac{d\beta}{d\alpha} = \frac{R \alpha}{\beta} \frac{d\beta}{d\alpha},$$

where $\alpha T_c = T$, and $\beta p_c = p$. Thus the relation between L_1 , T , and m for different liquids at corresponding states is given by $\frac{L_1 m}{T} = \text{constant}$. Since the temperatures of liquids at their boiling-points are approximately corresponding temperatures, this relation holds approximately for liquids at their boiling-points; it is known in this form as Trouton's law. If the temperature of evaporation is so far removed from the critical temperature that the vapour behaves approximately as a perfect gas, the external work of evaporation $p(v_1 - v_2)$ is approximately equal to $\frac{RT}{m}$. Therefore

$$L + p(v_1 - v_2) = L + \frac{RT}{m} = L_1$$

and therefore $\frac{L_1 m}{T} = \frac{L m}{T} + R = \text{constant}$, or $\frac{L m}{T}$ is also

constant for different liquids at corresponding states. Writing $\frac{Lm}{T} = B$, where $B = \frac{R\alpha}{\beta} \frac{d\beta}{d\alpha} - R$, and substituting for L in equation (4) we obtain

$$K = \frac{\rho^{2/3} A (T_c - a) m^{1/3}}{T^2 B}.$$

Expressing ρ and T in terms of the critical density and temperature, we obtain

$$K = \frac{A \gamma^{2/3} \rho_c^{2/3} (T_c - a) m^{1/3}}{B \alpha^2 T_c^2},$$

where $\rho = \gamma \rho_c$.

Let us write the equation in the form

$$K = \frac{M m^{1/3} (T_c - a) \rho_c^{2/3}}{T_c^2},$$

where $M = \frac{A}{B} \frac{\gamma^{2/3}}{\alpha^2}$. Now it is known that K is a constant

for a given liquid, therefore M must be a constant for the liquid. Further, in obtaining K for different liquids we may suppose the liquids taken at corresponding states, so that the values of α, β, γ , are the same for each liquid. Then it follows that since M is a function of α, β , and γ only, it must be the same for each liquid.

Further, since a is equal to about 5 and T_c of the order 500, $\frac{a}{T_c^2}$ may be neglected in comparison with $\frac{1}{T_c}$. We have then, finally,

$$K = \frac{M m^{1/3} \rho_c^{2/3}}{T_c}, \quad . \quad . \quad . \quad (5)$$

where M is a constant which is the same for every liquid.

The following table contains the values of $10^4 \frac{M m^{1/3} \rho_c^{2/3}}{T_c}$ for a few liquids calculated from the data given in the second, third, and fourth columns of the table, the value of M being put equal to 5.57×10^{-1} in each case. The values of $10^4 K$, contained in the fifth column of the table, are the means of the values contained in the preceding tables. It will be seen that the values of K given by equation (5) agree fairly well with the values given by the equation $K = \frac{E}{L T}$. A better agreement can scarcely be expected since the critical constants cannot be determined with any great accuracy.

$M = 5.57 \times 10^{-1}$.					
	T_c	ρ_c	m	$K10^4$	$\frac{10^4 M m^{1/3} \rho_c^{2/3}}{T_c}$
Ether	466.6	.2604	74	20.5	20.4
Methyl formate	487	.3489	60	21.2	22.2
Carbon tetrachloride ...	556	.5576	153.8	38.1	36.4
Benzene	561.5	.3045	78.05	19.5	19.2
Chloro-benzene	633	.3654	112.5	21.2	21.7

The value of K given by equation (4) will not apply to polymerized liquids because the value of A is then not a constant, but varies with the nature of the liquid and its temperature. It is also very probable that the relation given by Whittaker does not apply to such liquids.

If the critical density and temperature of a liquid is known, and its capillary constants for temperatures differing by a small interval, the internal latent heat can be calculated for these temperatures by the equation

$$L = \left(\frac{\lambda}{T} - \frac{d\lambda}{dT} \right) \frac{T_c}{m^{1/3} \rho_c^{2/3}} \frac{1}{5.57 \times 10^{-1}},$$

deduced from the equations (1), (2), and (5). An inspection of Whittaker's results shows that K or $\frac{E}{LT}$ is very constant for different temperatures, and this equation would therefore give fairly accurate results.

If a large number of determinations of λ for different temperatures are not available, the values of λ and $\frac{d\lambda}{dT}$ in the above equation may be obtained from equation (2), the constants in the equation having first been determined by means of the values of λ for two different temperatures. This, however, will not give very accurate values for L .

Equation (5), by writing it in the form

$$\frac{E}{LT} = \frac{M m^{1/3} \rho_c^{2/3}}{T_c},$$

may be used to find either of the critical constants it contains if one of them is known. The right-hand side may be evaluated for any convenient temperature.

Cambridge, March 20, 1909.