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**XL. Relations between the Density, Temperature, and Pressure of Substances.** By R. D. KLEEMAN, D.Sc., B.A., Mackinnon Student of the Royal Society\*.

THE writer† has shown in a previous paper that an infinite number of equations can be found connecting the surface tension or latent heat of evaporation of a liquid with its temperature and density and density of the saturated vapour. These equations correspond to laws of attraction between the molecules, but none of which is necessarily the law that actually exists. Each of these laws can be obtained by giving a definite value to the arbitrary function contained in the general law of attraction that can be deduced from surface tension or latent heat data. This general law of attraction between two molecules of the same kind is  $\phi_2\left(\frac{z}{x_c}, \frac{T}{T_c}\right) \cdot \frac{(\Sigma \sqrt{m_1})^2}{z^5}$ , where T denotes the temperature of the molecules and z their distance of separation,  $x_c$  denotes their distance of separation in the liquid state at the temperature  $T_c$ ,  $\Sigma \sqrt{m_1}$  denotes the sum of the square roots of the atomic weights of the atoms in a molecule, and  $\phi_2\left(\frac{z}{x_c}, \frac{T}{T_c}\right)$  denotes an arbitrary function of  $\frac{T}{T_c}$  and  $\frac{z}{x_c}$ .

There exists, therefore, an infinite series of equations of the form  $L = \psi_1(\rho_1, \rho_2, T) = \psi_2(\rho_1, \rho_2, T) = \dots$ , where L denotes the internal heat of evaporation of a liquid at the temperature T, and  $\rho_1$  and  $\rho_2$  denote the density of the liquid and that of the saturated vapour respectively. It is obvious that we can obtain from these equations an infinite number of equations containing T,  $\rho_1$ , or  $\rho_2$  only. Now each of the equations thus obtained must obviously be either an identity or be an equation which has an infinite number of real positive roots lying between certain limits. In practice, however, the equations found in the above way (usually by trial) do not exactly satisfy these conditions. But this is of no consequence, as the equations deduced, containing any two of the quantities  $\rho_1$ ,  $\rho_2$ , T, usually agree very well with the facts. It is the object of this paper to point out and discuss some of these equations.

Mills‡ has shown that the internal latent heat of evaporation is very approximately given by the equation  $L = D(\rho_1^{1/3} - \rho_2^{1/3})$ , where D is a constant depending only on

\* Communicated by the Author.

† Phil. Mag. Jan. 1911, p. 83.

‡ Journ. of Phys. Chem. vol. viii. p. 405 (1904).

the nature of the liquid. The writer\* has shown that this equation can be deduced if  $\phi_2\left(\frac{\rho_1}{\rho_2}, \frac{T_c}{T}\right)$  is put equal to  $\left(\frac{z}{x_c}\right)^3$  in the general law of attraction between molecules. We then obtain  $D = \frac{S\rho_c}{m^{4/3}}(\Sigma \sqrt{m_1})^2$ , where  $m$  denotes the molecular weight of the liquid,  $\rho_c$  the critical density, and  $S$  a numerical constant. This value of  $D$  agrees fairly well with the facts. The latent heat is also given by the equation †

$$L = \frac{K_4 RT}{m} \log\left(\frac{\rho_1}{\rho_2}\right),$$

where  $K_4$  is a numerical constant equal to about 1.75; which also corresponds to a particular case of the general law of attraction between molecules. Equating these two different equations for the latent heat we obtain

$$B(\rho_1^{1/3} - \rho_2^{1/3}) = T \log\left(\frac{\rho_1}{\rho_2}\right),$$

where

$$B = \frac{S\rho_c}{K_4 R m^{4/3}} (\Sigma \sqrt{m_1})^2.$$

Another expression for  $B$  which is convenient can be obtained by determining  $B$  at the critical temperature from the first of the above two equations. Writing  $\rho_2 = x\rho_1$  we have

$$B = \left[ \frac{T \log \frac{1}{x}}{\rho_1^{1/3}(1-x^{1/3})} \right]_{T=T_c, x=1} = \frac{3T_c}{\rho_c^{1/3}};$$

and the above equation becomes

$$\frac{3T_c}{\rho_c^{1/3}}(\rho_1^{1/3} - \rho_2^{1/3}) = T \log\left(\frac{\rho_1}{\rho_2}\right). \quad \dots \quad (1)$$

If the two different expressions obtained for  $B$  are equated we get

$$T_c = \frac{S}{3K_4 R} \left(\frac{\rho_c}{m}\right)^{4/3} (\Sigma \sqrt{m_1})^2,$$

an equation which has already been discussed in previous papers.

Equation (1) has many useful applications, and it has therefore been tested over considerable ranges of temperature for a number of liquids in Table I., which contains the values of  $\frac{10^4}{B}$  calculated by means of this equation. The

\* *Loc. cit.*

† *Phil. Mag.* Oct. 1910, p. 688.

TABLE I.

Ethyl oxide, $C_2H_5O$ .		Pentane, $C_5H_{12}$ .		Stannic chloride, $SnCl_4$ .		Octane, $C_8H_{18}$ .		Benzene, $C_6H_6$ .		Heptane, $C_7H_{16}$ .	
T.	$\frac{10^4}{B}$ .	T.	$\frac{10^4}{B}$ .	T.	$\frac{10^4}{B}$ .	T.	$\frac{10^4}{B}$ .	T.	$\frac{10^4}{B}$ .	T.	$\frac{10^4}{B}$ .
273	4.36	273	4.21	373	4.96	273	3.02	273	3.76	273	3.35
293	4.42	313	4.29	393	4.99	393	3.42	353	3.95	353	3.60
313	4.46	333	4.29	413	5.01	413	3.44	373	3.96	373	3.63
333	4.48	353	4.29	433	5.02	433	3.44	393	3.97	393	3.65
353	4.49	373	4.29	453	5.02	453	3.46	413	3.96	413	3.66
373	4.42	393	4.28	473	5.02	473	3.46	433	3.95	433	3.67
393	4.48	413	4.27	493	5.01	493	3.47	453	3.93	453	3.67
413	4.46	433	4.27	513	4.99	513	3.48	473	3.92	473	3.68
433	4.47	453	4.27	533	5.04	533	3.48	493	3.91	493	3.68
453	4.48	463	4.29	553	4.99	552	3.52	513	3.90	513	3.68
460	4.54	468	4.33					533	3.91	533	3.74
466	4.56	469	4.31					553	3.93	539	3.78
Iodo- benzene, $C_6H_5I$ .		Bromo- benzene, $C_6H_5Br$ .		Hexane, $C_6H_{14}$ .		Carbon tetrachloride, $CCl_4$ .		Di- isobutyl, $C_8H_{18}$ .		Ethyl acetate, $C_4H_8O_2$ .	
303	3.39	403	3.31	273	3.74	273	4.15	273	3.26	273	3.31
473	3.63	533	3.84	343	3.92	373	4.94	373	3.56	363	4.09
563	3.80	553	3.85	363	3.94	393	4.94	393	3.60	383	4.11
583	3.80	573	3.85	383	3.94	413	4.93	413	3.62	403	4.13
603	3.80	593	3.85	403	3.94	433	4.91	433	3.62	423	4.14
623	3.81	613	3.85	423	3.94	453	4.89	453	3.63	443	4.15
643	3.81	633	3.85	443	3.94	473	4.87	473	3.62	463	4.15
				463	3.94	493	4.85	493	3.62	483	4.16
				483	3.95	513	4.83	513	3.64	503	4.19
				499	3.97	533	4.84	533	3.66	518	4.28
				506	4.01	553	4.87	547	3.71	522	4.27
Chloro- benzene, $C_6H_5Cl$ .		Carbon dioxide, $CO_2$ .		Acetone, $C_3H_6O$ .		Chloroform, $CHCl_3$ .		Fluor- benzene, $C_6H_5F$ .		Hexa- methylene, $C_6H_{12}$ .	
273	3.34	243	8.30	273	3.93	293	4.89	273	3.89	273	3.70
413	3.70	263	8.38	293	3.98	313	4.94	353	4.11	363	3.87
433	3.71	283	8.30	313	4.02	333	4.98	373	4.13	383	3.89
453	3.71	298	8.44	333	4.05			393	4.14	403	3.89
473	3.71							413	4.15	423	3.88
493	3.71							433	4.15	443	3.87
513	3.70							453	4.14	463	3.85
533	3.69							473	4.13	483	3.84
Methyl formate, $C_2H_4O_2$ .		Sulphur dioxide, $SO_2$ .		Ethyl formate, $C_3H_6O_2$ .		Ethyl propionate, $C_5H_{10}O_2$ .					
303	4.66	263	6.12	333	4.35	383	3.85	493	4.12	503	3.83
323	4.72	283	6.18	353	4.38	433	3.90	513	4.11	523	3.83
363	4.73	303	6.19	393	4.40	453	3.91	533	4.11	543	3.84
403	4.72	323	6.26	413	4.40	473	3.92	553	4.15	552	3.88
443	4.71	343	6.21	433	4.40	493	3.93				
		363	6.15	473	4.40	513	3.94				
		383	6.15	493	4.41	533	3.98				
		403	6.16	507	4.47	541	4.00				
		418	6.19								
		428	6.28								

complete data used for these calculations and others in this paper can be obtained from the tables of density and pressure data of Ramsay and Young given in papers by Mills\*; part of the data (taken from this source) can be obtained from a previous paper by the writer†. It will be seen that the value of  $\frac{10^4}{B}$  is very approximately independent of the temperature for each liquid. Table II. contains the mean values

TABLE II.

Name of substance.	$\frac{B}{10^4}$	$\frac{3T_c}{10^3 \rho_c^{1/3}}$	$\psi_1(T)$	$\frac{\rho_c^{1/3}}{3}(3 - \log \rho_c)$	E.	$\frac{T_c}{\rho_c^{2/3} \times 2 \cdot 303}$
Ethyl oxide .....	2.24	2.20	.930	.931	1507	1496
Pentane .....	2.33	2.29	.912	.916	1951	1940
Stannic chloride ...	2.00	1.96	1.08	1.29	237	233.4
Octane .....	2.88	2.78	.916	.914	2393	2282
Benzene .....	2.54	2.51	.950	.939	1357	1316
Heptane .....	2.72	2.63	.914	.915	2246	2138
Iodo-benzene.....	2.64	2.59	1.08	1.22	463.4	462.9
Bromo-benzene.....	2.60	2.56	1.03	1.23	621.0	617.7
Hexane .....	2.53	2.47	1.07	.914	2094	2011
Carbon tetrachloride	2.05	2.03	1.02	1.27	403.7	388.2
Di-isobutyl .....	2.76	2.64	.918	.915	2247	2109
Ethyl acetate.....	2.40	2.35	.952	.938	1239	1266
Chlorobenzene .....	2.70	2.66	.983	.977	1049	1118
Carbon dioxide .....	1.20	1.43	.931	.972	322.7	306.8
Acetone .....	2.51	...	.953	...	...	...
Chloroform .....	2.02	...	1.09	...	...	...
Fluor-benzene .....	2.42	2.37	.972	.953	1001	968.7
Hexamethylene.....	2.61	2.54	1.23	.929	1661	1604
Sulphur dioxide ...	1.61	...	1.05	...	...	...
Ethyl formate .....	2.13	2.23	1.00	.942	1092	1102
Ethyl propionate ...	2.62	2.48	.933	.934	1410	1447
Methyl formate.....	2.12	2.07	.969	.951	893.9	869.0

of  $\frac{B}{10^3}$  of each liquid and the corresponding values of  $\frac{3T_c}{10^3 \rho_c^{1/3}}$ . The agreement between the two sets of values is very good. The values of  $\rho_c$  and  $T_c$  used to calculate the value of the above expression are given in Table IV.

Several results of interest and usefulness may be deduced from equation (1). It may be expressed as two equations thus :

$$\rho_1^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_1 = \psi_1(T), \quad \rho_2^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_2 = \psi_1(T),$$

where  $\psi_1(T)$  is an appropriate function of  $T$ . Now it was found

\* Journ. Phys. Chem. vol. viii. p. 405 (1904).

† Phil. Mag. Oct. 1910, pp. 679-681.

that  $\psi_1(T)$  is approximately a constant for each substance, and that it varies very little from substance to substance. This is shown by Table III., which contains the values of

TABLE III.

Ethyl acetate.		Hexa-methylene.		Carbon tetrachloride.		Bromo-benzene.		Heptane.		Benzene.	
T.	$\psi_1(T)$ .	T.	$\psi_1(T)$ .	T.	$\psi_1(T)$ .	T.	$\psi_1(T)$ .	T.	$\psi_1(T)$ .	T.	$\psi_1(T)$ .
363	.977	273	1.02	373	1.05	533	1.05	353	.933	353	.961
383	.969	363	1.07	393	1.04	553	1.04	373	.926	373	.955
403	.962	383	1.17	413	1.04	573	1.03	393	.921	393	.951
423	.957	403	1.24	433	1.03	593	1.03	413	.917	413	.950
443	.953	423	1.27	453	1.03	613	1.02	433	.915	433	.950
463	.949	443	1.30	473	1.02	633	1.01	453	.914	453	.951
483	.945	463	1.32	493	1.02	Iodo-benzene.		473	.914	473	.951
503	.940	483	1.32	513	1.01			493	.913	493	.950
518	.934	503	1.32	533	1.00			513	.911	513	.948
522	.932	523	1.30	553	.988			533	.907	533	.945
		543	1.26					539	.904	553	.940
		552	1.22								
Fluor-benzene.		Octane.		Stannic chloride.		473 1.17 563 1.08 583 1.07 603 1.06 623 1.06 643 1.05		Hexane.		Di-isopropyl.	
353	.995	393	.928	373	1.14			343	1.12	323	.922
373	.987	413	.922	393	1.12			363	1.11	343	.915
393	.982	433	.919	413	1.10			383	1.10	363	.916
413	.976	453	.916	433	1.09			403	1.09	383	.915
433	.974	473	.915	453	1.08	Chloro-benzene.		423	1.08	383	.915
453	.971	493	.913	473	1.06			443	1.06	403	.916
473	.967	513	.911	493	1.06			463	1.05	423	.919
493	.967	533	.910	513	1.05			483	1.04	443	.918
513	.963	553	.906	533	1.04	533	.973	499	1.02	463	.919
533	.959			553	1.02			506	1.00	483	.917
553	.952									493	.916
Methyl formate.		Ethyl propionate.		Ethyl oxide.		413 .995 433 .990 453 .985 473 .982 493 .979 513 .976 533 .973		Pentane.		Di-isobutyl.	
323	.991	383	.950	293	.945			313	.913	323	.936
403	.968	423	.937	353	.929			353	.911	343	.925
483	.949	463	.930	413	.928			373	.911	363	.919
		500	.926	460	.919			393	.913	393	.916
		538	.920					433	.914	423	.915
								453	.913	453	.914
								463	.912	483	.911
								469	.909	498	.906
Ethyl formate.		Carbon dioxide.		Sulphur dioxide.		273 1.13 330 1.06		Propyl formate.			
333	1.04	243	1.01	283	1.06			373	.968		
393	1.01	298	.973	323	1.03			433	.955		
433	1.00			363	1.02			493	.947		
507	.961			403	1.00						

$\psi_1(T)$  at different temperatures for a number of liquids, the latter of the above equations being used for calculating  $\psi_1(T)$ . The slight deviations of  $\psi_1(T)$  from constancy are regular, there being a slight decrease in its value with the temperature.

The value of  $\psi_1(T)$  in terms of the critical constants, obtained by substituting for the quantities  $T$ ,  $\rho_1$ , and  $\rho_2$  in either of the equations their critical values, is

$$\frac{\rho_c^{1/3}}{3} (3 - \log \rho_c).$$

The above equations may thus be written:

$$\left. \begin{aligned} \rho_1^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_1 &= \frac{\rho_c^{1/3}}{3} (3 - \log \rho_c), \\ \rho_2^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_2 &= \frac{\rho_c^{1/3}}{3} (3 - \log \rho_c). \end{aligned} \right\} \quad \cdot \quad (2)$$

Table II. contains the mean value of  $\psi_1(T)$  for each liquid contained in Table III., and the corresponding values of

$$\frac{\rho_c^{1/3}}{3} (3 - \log \rho_c).$$

The agreement between the two sets of values is fairly good.

Since the equations (2) are the same in form, for a given temperature each must have at least two real positive roots, one being equal to the value of  $\rho_1$  and the other to the value of  $\rho_2$ .

An expression for  $\frac{d\rho_1}{dT}$  is obtained by differentiating the first of equations (2), which gives

$$\frac{d\rho_1}{dT} = \frac{\rho_1 \rho_c^{1/3} \log \rho_1}{T_c \rho_1^{1/3} - T \rho_c^{1/3}}.$$

It will be seen that at the critical temperature  $\frac{d\rho_1}{dT} = \infty$ , a result that has already been established by thermodynamics.

At the absolute zero  $\frac{d\rho_1}{dT}$  is finite. For intermediate temperatures the equation gives values of  $\frac{d\rho_1}{dT}$  which agree roughly with the facts. That a good agreement is not obtained is due to  $\psi_1(T)$  being only approximately a constant. A better agreement would be obtained by writing  $\psi_1(T) = a - Tb$ , when we obtain

$$\frac{d\rho_1}{dT} = \frac{\rho_1 \rho_c^{1/3} \log \rho_1 - 3T_c \rho_1 b}{T_c \rho_1^{1/3} - \rho_c^{1/3} T}.$$

The value of  $b$  is best obtained from this equation by applying it to a case when all the quantities it contains are known except  $b$ .

We may substitute  $\rho_2$  for  $\rho_1$  in the above equations. It can then be easily shown that at the absolute zero  $\frac{d\rho_2}{dT} = -\infty$ .

Let us express the quantities  $\rho_1$ ,  $\rho_2$ , and  $T$  in terms of their critical values thus,  $\rho_1 = \rho_c n_1$ ,  $\rho_2 = \rho_c n_2$ ,  $T = T_c n_3$ , and substitute in equation (1). The equation reduces to

$$\frac{n_3}{3} \log \frac{n_1}{n_2} = n_1^{1/3} - n_2^{1/3}, \quad . \quad . \quad . \quad (3)$$

which, it will be seen, is independent of the nature of the liquid under consideration. Since  $\rho_1$  and  $\rho_2$  are each a function of  $T$ , and  $n_1$  and  $n_2$  therefore each a function of  $n_3$ , it follows that for equal values of  $n_3$  for a number of substances,  $n_1$  and  $n_2$  will each have equal values. The equation thus demonstrates the theory of corresponding states, and gives a relation between the quantities  $n_1$ ,  $n_2$ ,  $n_3$ . The corresponding state of substances, it will be shown later, has its fundamental reason in the occurrence of the function in the general law of attraction between molecules which has the same value for all substances at corresponding temperatures.

In a previous paper\* we have established the relation  $E(\rho_1^2 - \rho_2^2) = T \log \frac{\rho_1}{\rho_2}$ , where  $E$  is a constant depending only on the nature of the liquid. This equation, like equation (1), represents two different formulæ for the latent heat equated. It was found to agree very well with the facts. The value of  $E$ , when the logarithm in the equation is taken to the base 10, was shown to be given by

$$\frac{258.8 (\sum \sqrt{m_1})^2}{m^{4/3} \rho_c^{2/3}}.$$

A different expression for  $E$  can be obtained in the same way as was obtained for  $B$ . Writing  $\rho_2 = x\rho_1$ , the value of  $E$  at the critical temperature is

$$\left[ \frac{T \log \frac{1}{x}}{\rho_1^2 (1 - x^2)} \right]_{Lx=1} = \frac{T_c}{2\rho_c^2}, \text{ or } \frac{T_c}{\rho_c^2 2 \times 2.303},$$

\* Phil. Mag. Oct. 1910, pp. 686-687.



if the logarithm is taken to the base 10. The equation may now be written

$$\frac{T_c}{\rho_c^2}(\rho_1^2 - \rho_2^2) = T \log \frac{\rho_1}{\rho_2} \quad (4)$$

The mean values of  $E$  for a number of substances, given by the above equation, and the corresponding values of

$\frac{T_c}{\rho_c^2 \times 2.303}$ , are given in Table II. The agreement between the two sets of values is fairly good.

From equations (1) and (4) we have

$$(\rho_1^2 - \rho_2^2) = 6 \rho_c^{5/3} (\rho_1^{1/3} - \rho_2^{1/3}). \quad (5)$$

If we, as before, express the quantities in this equation in terms of their critical values, we have

$$n_1^2 - n_2^2 = 6 (n_1^{1/3} - n_2^{1/3}). \quad (6)$$

Equations (1) and (5) express approximately the relation between the quantities  $\rho_1$ ,  $\rho_2$ , and  $T$ , and equations (3) and (6) the relation between the quantities  $n_1$ ,  $n_2$ , and  $n_3$ .

Equations (1) and (5) are very useful. From equation (5) we have  $\rho_c = \left( \frac{\rho_1^2 - \rho_2^2}{6\rho_1^{1/3} - 6\rho_2^{1/3}} \right)^{3/5}$ , which may be used to calculate

TABLE IV.

Name of liquid.	T.	$\rho_1$ .	$\rho_2$ .	$\rho_c$ (Landolt & Börnstein).	$\left\{ \frac{\rho_1^2 - \rho_2^2}{6\rho_1^{1/3} - 6\rho_2^{1/3}} \right\}^{3/5}$	$T_c$ (Landolt & Börnstein).	$\frac{B\rho_c^{1/3}}{3}$
Ethyl oxide .....	293	·7135	·00187	·2604	·2661	467·4	484·8
Octane .....	323	·6168	·0033	·2327	·2243	569·2	592·4
Ethyl propionate ..	383	·7823	·004739	·2860	·3011	545·4	580·1
Pentane .....	313	·6062	·00339	·2323	·2505	470·0	489·8
Benzene .....	353	·8145	·002722	·3045	·3071	561·5	569·4
Heptane .....	353	·6311	·001996	·2341	·2343	539·9	570·7
Hexane .....	343	·6122	·00337	·2344	·2347	507·8	524·7
Carbon tetrachloride	373	1·4343	·01026	·5576	·5563	556·1	555·0
Iodo-benzene .....	473	1·7079	·0,4400	·5814	·5755	721	729·3
Bromo-benzene .....	433	1·2994	·005255	·4853	·4919	670	684·4
Di-isobutyl .....	373	·6236	·002967	·2366	·2125	543·8	558·4
Ethyl acetate .....	363	·8112	·004673	·2993	·3076	522·5	550·3
Fluor-benzene .....	353	·9496	·002885	·3541	·3559	559·5	575·0
Carbon dioxide .....	263	·9560	·0725	·464	·4606	304·3	307·0
Hexamethylene .....	363	·7106	·003759	·2735	·2721	553	558·0
Chloro-benzene .....	413	·9723	·004316	·3654	·3695	633	646·8
Methyl formate .....	303	·9598	·002225	·3489	·3567	487	477·7
Ethyl formate .....	333	·8659	·003356	·3150	·3360	503	525·5

the critical density of a liquid from any available density data. The critical densities of a number of liquids have been calculated by means of this equation and are contained in Table IV., which contains also the data used. The agreement between these values and the critical densities given in Landolt and Börnstein's Tables, 5th edition, which are also given in Table IV., is quite good. The formula should always give a fairly accurate value of  $\rho_c$ , since its form is such that the percentage error in the value of  $\rho_c$  caused by errors in the values of  $\rho_1$  or  $\rho_2$  is not in most cases larger than the percentage error in the latter quantities.

Equation (1) gives the value of B or  $\frac{3T_c}{\rho_c^{1/3}}$ , which enables us to calculate  $T_c$  if  $\rho_c$  is known. The values of  $T_c$  or  $B\rho_c^{1/3}$  have been calculated in this way for a number of substances, and are given in Table IV., using the values of  $\rho$  previously found, and calculating B by means of the data used for calculating  $\rho_c$ . The agreement of these values of  $T_c$  with those taken from Landolt and Börnstein's Tables is as good as can be expected. It will be observed that since the cube root of  $\rho_c$  occurs in the expression for  $T_c$ , the percentage error in the value of  $\rho_c$  introduces a much smaller percentage error in the value of  $T_c$ .

Further relations of interest can be deduced. We have seen that

$$L = 1.75 \frac{RT}{m} \log \frac{\rho_1}{\rho_2},$$

and we therefore have from equation (1) that the value of D in the equation

$$L = D (\rho_1^{1/3} - \rho_2^{1/3})$$

may be written

$$\frac{5.25RT_c}{m\rho_c^{1/3}}.$$

Substituting the value of L from the latter equation in Clapeyron's equation we have

$$\frac{dP}{dT} \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right) T = P \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right) + \frac{5.25RT_c}{m\rho_c^{1/3}} (\rho_1^{1/3} - \rho_2^{1/3}),$$

where P denotes the pressure of the saturated vapour.

We may express this equation in the form of two thus :

$$\left. \begin{aligned} \frac{dP}{dT} \frac{T}{\rho_1} &= \frac{P}{\rho_1} + \frac{5 \cdot 25 RT_c}{m \rho_c^{1/3}} \rho_1^{1/3} + \psi_2(T), \\ \frac{dP}{dT} \frac{T}{\rho_2} &= \frac{P}{\rho_2} + \frac{5 \cdot 25 RT_c}{m \rho_c^{1/3}} \rho_2^{1/3} + \psi_2(T). \end{aligned} \right\} \quad \dots \quad (6)$$

Now it was found that the value of  $\psi_2(T)$  is approximately constant for the same substance. This is shown for two substances in Table V.,  $\psi_2(T)$  being calculated by means of the latter of the above equations from the data given in the table.

TABLE V.

PENTANE.					HEXANE.				
T.	$\rho_2$ .	P in mm. of Hg.	$\frac{dP}{dT}$ .	$\psi_2(T)$ .	T.	$\rho_2$ .	P in mm. of Hg.	$\frac{dP}{dT}$ .	$\psi_2(T)$ .
313	003390	865.3	28.81	93.2	343	00337	784.8	24.73	89.7
333	006024	1601.8	46.19	90.1	363	00585	1409	38.80	87.2
353	01013	2742.1	69.37	93.5	383	00952	2358	57.20	86.8
373	01627	4409.1	99.05	91.9	403	01502	3723	80.55	85.9
393	02503	6740.5	136.02	92.1	423	02299	5606	109.2	85.2
413	03861	9890	181.1	91.4	443	03472	8123	144.0	84.2
433	05910	14032	235.4	91.0	463	05155	11407	186.3	84.1
453	09354	19362	300.2	90.6	483	07900	15619	237.4	83.6

The constancy of  $\psi_2(T)$  can be tested more conveniently by means of the equation obtained by eliminating  $\left(\frac{dP}{dT} - P\right)$  from equations (6). We thus obtain

$$C(\rho_1^{4/3} - \rho_2^{4/3}) = \rho_1 - \rho_2, \text{ where } C = \frac{5 \cdot 25 RT_c}{m \rho_c^{1/3} \cdot \psi(T)}.$$

It follows, therefore, that if it is found that  $C$  is independent of the temperature for a substance, then  $\psi_2(T)$  must possess the same property. Now this is approximately realized, as will appear from Table VI., which contains the values of  $C$  at different temperatures for a number of substances.

We can find another expression for the value of  $C$ , which enables us to obtain an expression for the value of  $\psi_2(T)$ . Let us write  $\rho_2 = x\rho_1$  in the above equation. and the value of

C is given by

$$C = \left[ \frac{1}{\rho_1^{1/3}} \left( \frac{1-x}{1-x^{4/3}} \right) \right]_{\text{Ltr}=1} = \frac{4}{3\rho_c^{1/3}}.$$

The above equation may then be written

$$\frac{3}{4\rho_c^{1/3}} (\rho_1^{4/3} - \rho_2^{4/3}) = \rho_1 - \rho_2. \quad . \quad . \quad . \quad (7)$$

We have also

$$\frac{3}{4\rho_c^{1/3}} = \frac{5.25RT_c}{m\rho_c^{1/3}\psi_2(T)}, \text{ and hence } \psi_2(T) = \frac{7RT_c}{m}.$$

In the case of pentane and hexane we obtain for  $\psi_2(T)$  from this equation the values 90.3 and 90.6 respectively, which agree fairly well with 91.7 and 85.8, the mean values of  $\psi_2(T)$  obtained from Table V.

The mean value of  $\frac{1}{C}$  for each substance is given at the bottom of Table VI. The agreement with the corresponding values of  $\frac{4}{3}\rho_c^{1/3}$  is fairly good. But it will be noticed that equation (7) does not on the whole agree so well with the facts as either equation (1) or (5).

TABLE VI.

Methyl butyrate.		Heptane.		Di-isobutyl.		Hexane.		Hexa-methylene.		Carbon tetrachloride.	
T.	$\psi_2(T)$ .	T.	$\psi_2(T)$ .	T.	$\psi_2(T)$ .	T.	$\psi_2(T)$ .	T.	$\psi_2(T)$ .	T.	$\psi_2(T)$ .
383	.930	273	.694	363	.861	333	.857	363	.897	273	1.18
403	.923	353	.702	383	.855	353	.849	383	.890	373	1.14
423	.916	373	.707	403	.848	373	.845	403	.884	393	1.13
443	.909	383	.707	423	.843	393	.837	423	.876	413	1.12
463	.903	393	.705	443	.836	413	.831	443	.874	433	1.11
483	.898	413	.701	463	.832	433	.826	463	.869	453	1.11
503	.894	433	.693	483	.827	453	.823	483	.866	473	1.10
523	.890	453	.677	503	.823	473	.820	503	.863	493	1.10
543	.890	473	.662	523	.822	493	.818	523	.861	513	1.09
551	.888			543	.822	503	.820	543	.862	533	1.13
Mean	.924		.695		.837		.833		.874		1.12
$\frac{3}{4}\rho_c^{1/3}$	.884		.822		.825		.822		.866		1.38

*General Considerations.*

We will now deduce some further results of a general nature from the law of attraction between molecules quoted at the beginning of the paper.

It can be easily shown that the theory of corresponding states follows from the law quoted. It will first be proved in the case of a liquid in contact with its saturated vapour. The equation for the internal latent heat of evaporation deduced from the law\* is

$$L = A_1 \frac{\rho_1^{4/3}}{m^{1/3}} (\Sigma \sqrt{m_1})^2 - A_2 \frac{\rho_2^{4/3}}{m^{1/3}} (\Sigma \sqrt{m_1})^2,$$

where

$$A_1 = \phi_3\left(\frac{x_a}{x_c}, \frac{T}{T_c}\right), \quad A_2 = \phi_3\left(\frac{x_b}{x_c}, \frac{T}{T_c}\right),$$

and  $x_a, x_b$  denote the distances of separation of the molecules in the liquid and gaseous state respectively. The form of  $A_1$  and  $A_2$ , it should be noticed, depends only on the form of the expression  $\phi_2\left(\frac{z}{x_c}, \frac{T}{T_c}\right)$  occurring in the law of attraction. We have seen that an infinite number of formulæ for the latent heat can be obtained which correspond to different forms of  $\phi_2$ , and there exists, therefore, a series of equations of the form

$$\begin{aligned} L &= A_1' \frac{\rho_1^{4/3}}{m^{1/3}} (\Sigma \sqrt{m_1})^2 - A_2' \frac{\rho_2^{4/3}}{m^{1/3}} (\Sigma \sqrt{m_1})^2 \\ &= A_1'' \frac{\rho_1^{4/3}}{m^{1/3}} (\Sigma \sqrt{m_1})^2 - A_2'' \frac{\rho_2^{4/3}}{m^{1/3}} (\Sigma \sqrt{m_1})^2 = \dots, \end{aligned}$$

or

$$\phi_4\left(\frac{x_a}{x_c}, \frac{T}{T_c}\right) - \phi_5\left(\frac{x_a}{x_c}, \frac{T}{T_c}\right) = \left\{ \phi_4\left(\frac{x_b}{x_c}, \frac{T}{T_c}\right) - \phi_5\left(\frac{x_b}{x_c}, \frac{T}{T_c}\right) \right\} \left(\frac{\rho_2}{\rho_1}\right)^{4/3} = \dots,$$

where  $\frac{x_a}{x_c} = \frac{\rho_1}{\rho_c}$ , and  $\frac{x_b}{x_c} = \frac{\rho_2}{\rho_c}$ .

It will be readily seen that if we express the quantities  $\rho_1, \rho_2$ , and  $T$  in terms of their critical values in the same way as before, the equations will contain  $n_1, n_2$ , and  $n_3$ , only. Since it must be possible to express  $n_1$  and  $n_2$  in terms of  $n_3$ , therefore if  $n_3$  for a number of substances has equal values,  $n_1$  and  $n_2$  will each have equal values. This proves the theory of corresponding states from the general law of attraction for the quantities  $\rho_1, \rho_2$ , and  $T$ .

\* Phil. Mag. May 1910, pp. 798-794.

The above series of equations are the general fundamental equations connecting  $T$ ,  $\rho_1$ , and  $\rho_2$ , for a liquid in contact with its saturated vapour. Since they also contain  $\rho_c$  and  $T_c$ , they are the fundamental equations for determining these quantities from any convenient data. The equations we have been discussing, obtained by equating different formulæ for the internal latent heat, will readily be recognized as belonging to this type of equations.

Making use of the above result, the equation for the latent heat may be written

$$L = B^2 \frac{\rho_1^{4/3}}{m^{7/3}} (\Sigma \sqrt{m_1})^2,$$

when  $B$  is a constant which is the same for all liquids at corresponding states. It can then be easily shown \* by means of this equation that  $L = L_0 \eta$ , where  $L_0$  is the latent heat at the absolute zero, and  $\eta$  is a constant which is the same for all liquids at corresponding states; which establishes the required result in the case of the internal latent heat.

By means of the foregoing results and thermodynamics the law of corresponding states can be established for the pressure  $p$  of the saturated vapour of a liquid. If the value of  $L$  from the former of the above two latent heat equations is substituted in Clapeyron's equation, it can be reduced to the form

$$W (\Sigma \sqrt{m_1})^2 \left( \frac{\rho_1}{m} \right)^{7/3} = p - \frac{T}{T_c} p_c \dagger,$$

where  $W$  is the same for all liquids at corresponding temperatures. At the critical point the right-hand side becomes zero, and since  $\rho_1$  is finite at the critical point,  $W$  must also become zero. The limiting value of the ratio  $\frac{p - T p_c / T_c}{W}$

may be written  $p_c \cdot V_c$ , where  $V_c$  is a numerical constant, and the equation at the critical point becomes

$$p_c = \frac{1}{V_c} (\Sigma \sqrt{m_1})^2 \left( \frac{\rho_c}{m} \right)^{7/3}.$$

Combining this equation with the above equation we have

$$V_c W p_c \left( \frac{\rho_1}{\rho_c} \right)^{7/3} = p - \frac{T p_c}{T_c},$$

or  $p = n_4 p_c$ , where  $n_4$  is the same for corresponding temperatures, which is the required result.

\* Phil. Mag. June 1910, p. 845.

† Phil. Mag. Dec. 1909, p. 903.

The equation  $p = n_4 p_c$  is of theoretical importance, as  $n_4$  is a function of  $n_1, n_2, n_3$ , and the equation therefore gives the relation between  $p, \rho_1, \rho_2$ , and  $T$ . It could at once be written out if the exact form of the arbitrary function in the law of attraction were known. It will be of interest to develop the equation as far as possible. The value of  $n_4$  is  $(V_c W n_1^{7/3} + n_3)$ , from one of the above equations. Referring

again to the paper quoted above, we have  $W = N - \frac{T}{T_c} N_c$ , where  $N_c$  is a numerical constant, and

$$N = \frac{n_3}{n_1^{7/3}} \int \frac{B^2 n_1^{2/3}}{a n_3^2} \cdot dn_3,$$

where

$$a = \frac{1}{n_2} - \frac{1}{n_1} = \frac{n_1 - n_2}{n_1 n_2},$$

changing some of the symbols to those used in this paper. The quantity  $B^2$  which occurs in the equation for the latent heat is a function of  $n_1, n_2$ , and  $n_3$ ; its form would be known if that of the arbitrary function in the law of attraction were known. From the way it is obtained it is likely to be a series\*. Writing  $B^2 = \psi_3(n_1, n_2, n_3)$ , the above equation reduces to

$$p = \left\{ V_c \int \frac{\psi_3(n_1, n_2, n_3) \cdot n_2 n_1^{5/3}}{(n_1 - n_2) n_3^2} \cdot dn_3 + 1 - N_c V_c n_1^{7/3} \right\} n_3 p_c.$$

This can be changed into an equation involving  $\rho_1, \rho_2$ , and  $T$ , by means of the equations  $\rho_1 = n_1 p_c$ ,  $\rho_2 = n_2 p_c$ ,  $T = n_3 T_c$ . Thus the part of the right-hand side of the equation not under the integral sign at once reduces to

$$\frac{T p_c}{T_c} \left( 1 - N_c V_c \left( \frac{\rho_1}{\rho_c} \right)^{7/3} \right).$$

The quantities  $n_2, n_1$  under the integral sign can be expressed in terms of  $n_3$  by means of the results already obtained and the expression integrated, and  $\frac{T}{T_c}$  then substituted for  $n_3$ .

This cannot yet, however, be effected in practice since we do not yet know the exact form of the function  $\phi_2$ . Without performing this operation, the equation connecting the

\* Phil. Mag. May 1910, pp. 793-794.

quantities  $p$ ,  $\rho_1$ ,  $\rho_2$ ,  $T$ , may be written

$$p = \frac{T}{T_c} p_c \left( 1 - N_c V_c \left( \frac{\rho_1}{\rho_c} \right)^{7/3} \right) + \frac{T p_c}{\rho_c^{5/3}} \int \frac{\psi_3 \left( \frac{\rho_1}{\rho_c}, \frac{\rho_2}{\rho_c}, \frac{T}{T_c} \right) \cdot \rho_2 \rho_1^{5/3} \cdot dT}{(\rho_1 - \rho_2) T^2}.$$

The law of corresponding states can also be proved for all possible states of matter. From thermodynamics we have

$$\left( \frac{dQ}{dp} \right)_{T \text{ const.}} = T \left( \frac{dv}{dT} \right)_{p \text{ const.}}$$

where  $dQ$  is the amount of heat given out by a mass of matter of volume  $v$  at a temperature  $T$ , when the pressure changes by  $dp$ . Now  $Q = pv + u$ , where  $u$  is the internal energy of the substance. The internal energy we will take (as usual) equal to the internal heat of evaporation at constant temperature into a vacuum. According to the formula for the latent heat used in a previous part of the paper (deduced from the law of molecular attraction), this is for unit mass equal to

$$\phi_3 \left( \frac{x_d}{x_c}, \frac{T}{T_c} \right) \cdot \frac{\rho^{4/3}}{m^{7/3}} (\Sigma \sqrt{m_1})^2,$$

where  $x_d$  is the distance of separation of the molecules of the matter and  $\rho$  its density. This expression for the internal energy we will write for shortness  $HC\rho^{4/3}$ , where

$$C = \frac{(\Sigma \sqrt{m_1})^2}{m^{7/3}}.$$

We have then

$$\begin{aligned} \left( \frac{dQ}{dp} \right)_T &= v + p \frac{dv}{dp} + C \left( \frac{dH}{dp} \rho^{4/3} + \frac{4}{3} H \rho^{1/3} \frac{d\rho}{dp} \right) \\ &= \left[ v + \left( \frac{dv}{dp} \right) \left\{ p + C \left( \frac{dH}{dv} \frac{1}{v^{4/3}} - \frac{H}{3v^{7/3}} \right) \right\} \right]_T = T \left( \frac{dv}{dT} \right)_p. \end{aligned}$$

Let us express the quantities  $p$ ,  $v$ , and  $T$  in terms of their critical values thus

$$p = \phi p_c, \quad v = \alpha v_c, \quad T = \beta T_c.$$

The above equation may then be written

$$\left[ \alpha + \phi \cdot \left( \frac{d\alpha}{d\phi} \right) + \frac{C}{p_c v_c^{7/3}} \left( \frac{d\alpha}{d\phi} \right) \frac{1}{\alpha^{7/3}} \left( \frac{dH}{d\alpha} \cdot \alpha - \frac{4}{3} H \right) \right]_\beta = \beta \left( \frac{d\alpha}{d\beta} \right)_\phi,$$

or  $\frac{CD}{p_c v_c^{7/3}} = E$ , where  $D$  and  $E$  are functions of  $\alpha$ ,  $\beta$ , and  $\phi$ .



At the critical point, when  $\alpha=1$ ,  $\beta=1$ ,  $\phi=1$ , let the numerical limiting values of  $D$  and  $E$  be denoted by  $D_c$  and  $E_c$ , so that  $\frac{CD_c}{p_c v_c^{7/3}} = E_c$ . Eliminating  $v_c$ ,  $C$ , and  $p_c$ , we have  $\frac{D}{D_c} = \frac{E}{E_c}$ , an equation which contains the quantities  $\alpha$ ,  $\beta$ , and  $\phi$  only. This proves the law of corresponding states in general.

Meslin has shown (*C. R.* 116, 135, 1893) that if the equation of state contains as many constants as there are variables (*i. e.* three—volume, temperature, pressure), it can be reduced to an equation involving  $\alpha$ ,  $\phi$ , and  $\beta$  only, or the law of corresponding states applies in that case to substances. Since we have established the law in a different way, we deduce that the equation of state must contain three constants.

The equation 
$$\frac{CD_c}{p_c v_c^{7/3}} = E_c$$

on substituting for  $p_c$ ,  $V_c$ , and  $C$ , from the equations

$$p = \phi p_c, \quad v = \alpha v_c, \quad \text{and} \quad c = \frac{(\sum \sqrt{m_1})^2}{m^{7/3}},$$

may be written

$$p = M^2 \left( \frac{\rho}{m} \right)^{7/3} (\sum \sqrt{m_1}),$$

where  $M^2$  is the same for all substances at corresponding states. This equation we have previously obtained for a liquid in contact with its saturated vapour. We now see that it applies in general.

The equation

$$T_1 = H^2 \left( \frac{\rho_1}{m} \right)^{4/3} (\sum \sqrt{m_1})^2,$$

where  $H^2$  has the same value for all substances at corresponding states, was also previously shown to apply to a liquid in contact with its saturated vapour\*. Now if we substitute for the quantities  $T_1$ ,  $\rho_1$ , from the equations  $\rho_1 = a\rho$ ,  $T_1 = bT$ , where  $T$  and  $\rho$  refer to any given state of matter, we obtain the equation

$$T = H_a \left( \frac{\rho}{m} \right)^{4/3} (\sum \sqrt{m_1})^2,$$

\* The equation was deduced with the help of thermodynamics from the general law of attraction quoted at the beginning of the paper.

where  $H_a$  is the same for corresponding states. This follows since the above two equations may be written

$$n_1 p_c = a \alpha \rho_c, \quad \text{and} \quad n_3 T_c = b \beta T_c,$$

and therefore

$$a = \frac{n_1}{\alpha}, \quad \text{and} \quad b = \frac{n_3}{\beta},$$

or  $b$  and  $a$  have the same values at corresponding temperatures. Thus the equation in question is proved for all states of matter.

From this and the above equation we obtain  $p v = \frac{I R T}{m}$ , which applies to all states of matter, where  $I$  is the same at corresponding states.

The general equation of state can be deduced from one of the foregoing equations, but it is of a form which is not of any use. We have obtained

$$v + (p + k) \frac{\delta v}{\delta p} = T \frac{\delta v}{\delta T},$$

where

$$k = C \left( \frac{dH}{dv} \frac{1}{v^{4/3}} - \frac{4}{3} \frac{H}{v^{7/3}} \right),$$

and is therefore a function of  $v$  and  $T$ . This is a linear partial differential equation, and the Lagrangian subsidiary equations are therefore

$$\frac{dv}{v} = \frac{dT}{T} = \frac{dp}{p + k}.$$

An independent integral of these equations is  $\frac{v}{T} = A$ , and let the other be denoted by  $\psi_s(T, v, p) = B$ . Then an integral of the partial differential equation is given by

$$\psi_s \left( \frac{v}{T}, \psi_s(T, v, p) \right) = 0,$$

where  $\psi_s$  is an arbitrary function. One of the conditions which determines the form of the arbitrary function is that the equation must approximate to  $p v = \frac{RT}{m}$  when the matter is in the gaseous state and the pressure is lowered.

London, December 19, 1910.