XLII. The relations of pressure, temperature, and volume in saturated vapours

W.C. Unwin M. Inst. C.E.

Some of Dr. Alder Wright's recent work is thus open to criticism on account of his theoretical conclusions on the results of the comparison of his values with those found in the calorimeter. Another desideratum in his recent papers is the statement of the effects of temperature on the E.M.F. of his cells. Such measurements should always be made, especially since the publication of Prof. Helmholtz's mathematical researches already referred to.

This paper is only put forward as a preliminary investigation of the electromotive forces developed during the combination of zinc and iodine, and the difficulty of dealing with zinc iodide as a salt in solution must be my excuse for not producing final results on going over the ground for the first time.

XLII. *The Relations of Pressure, Temperature, and Volume in Saturated Vapours.* By W. C. UNWIN, *M. Inst. C.E.**

IN the interesting and laborious paper of Messrs. Ramsay and Young, there are given four relations of a simple kind between the pressures, temperatures, and volumes of saturated vapours and the heat of vaporization of a number of substances. These relations are not given as exact relations, but as suggestive of laws approximately satisfied by very different substances over a very wide range of conditions.

Now long ago Hirn pointed out that, as for saturated vapours there exists only a single value of p and t corresponding to one specific volume v, there must be a direct relation between t and v, and between p and v, independent of p or t. But hitherto no exact relation has been found, and we remain still in the condition of being obliged in every thermodynamical calculation to fall back at every step on data either interpolated from tables of experimental values, or determined by the aid of purely empirical formulæ. Nor is this all: the formulæ are themselves cumbrous and are not interrelated.

Regnault's formula, giving p in terms of t for instance, cannot be inverted to get t in terms of p, though in practical calculations the pressure is almost always the given datum. Further, if differentiated to obtain $\frac{dp}{dt}$ an expression is obtained far too cumbrous for ordinary use. Rankine's formula is nearly as accurate, and is both simpler and gives an inverse function; but the expression for $\frac{dp}{dt}$ is cumbrous. The expression for latent heat is necessarily independent, but then

* Communicated by the Physical Society; read February 27, 1886.

the density or specific volume ought to be expressed in terms of the formulæ for latent heat and pressure and temperature. But there being no simple expression for $\frac{dp}{dt}$ it is more common to resort to the quite independent empirical formula of Zeuner.

For purely scientific purposes no absolute difficulty or inaccuracy is caused, and no advance can be hoped for till rational expressions are found. When such expressions are found, also, it may probably prove, as Hirn surmises, that they will not have the simplicity which some people expect in all natural laws. The practical difficulty, again, can be surmounted by means of the tabulated values of p, t, $\frac{dp}{dt}$, calculated with great care and labour by Prof. Zeuner and Prof. Cotterill. Nevertheless the author thinks that some clearness would be introduced into the teaching of thermodynamics, and possibly some facility gained in practical calculations, if only amongst empirical expressions to which recourse must be had, one could be found accurate enough and yet so simple that all the related functions could be derived from it. The paper of Messrs. Ramsay and Young suggested an attempt in that direction.

It might be expected that the approximate relations stated by Profs. Ramsay and Young could be deduced from some of the empirical relations already established. This, however, is not strictly the case.

It is known for instance that the expression

$$p = A T^{5\cdot 5},$$

where A is a constant and T is reckoned from an arbitrary zero, approximately satisfies the law connecting the pressure and temperature of saturated vapours.

Differentiating,

$$\frac{dp}{dT} = 5\cdot 5 A\, T^{4\cdot 5},$$

So that

$$T\, \frac{dp}{dT} = 5\cdot 5 A\, T^{5\cdot 5} = 5\cdot 5 p.$$

Consequently

$$\frac{T}{p}\, \frac{dp}{dT} = 5\cdot 5:$$

a relation which should be approximately satisfied for different vapours.

Thus, for instance, reckoning from the zeros given below

we get from the values of $\dfrac{dp}{dt}$ in Messrs. Ramsay and Young's tables the following values of $\dfrac{T}{p}\dfrac{dp}{dt}$:—

Substance ... {	Bisulph. of Carbon.	Ethyl Alcohol.	Water.	Mercury.
Zero (Above −273°C) }	144°.	208°.	210°.	322°.
Pressure in mm.				
100	5·913	5·323	5·183	5·243
500	5·749	5·616	5·794	5·598
1000	5·666	5·802	5·808	5·707
5000	5·201	5·540	5·645	......
10,000	......	5·429	5·503	......
20,000	......	5·291	5·302	......

At first sight it looks as if this were similar to the relation $t\dfrac{dp}{dt}=$ constant at any one pressure, given in Messrs. Ramsay and Young's paper. But, obviously, it is a quite different relation from the difference in the reckoning of temperature. It is, besides, a purely empirical relation, and the constancy of the values obtained may serve as a useful warning against accepting such correspondence of formula and data as indicating that the formula expresses a real law.

The principal relation discussed by Messrs. Ramsay and Young is that

$$t\,\frac{dp}{dt}$$

is constant for different vapours at the same pressure. In their table (Proc. Phys. Soc. vol. vii. p. 301*) values of this quantity, very carefully and laboriously calculated, are given for various vapours at pressures ranging from 10 to 20,000 mm. of mercury. It will easily be seen that the numbers in each horizontal line in their table approximate to constancy, varying in extreme cases by possibly 30 per cent.

If now these numbers are divided by the pressures so as to form values of

$$\frac{t}{p}\,\frac{dp}{dt}$$

the constancy of the horizontal lines of figures will remain unaffected, while the vertical columns will approach to constancy almost as nearly as the horizontal columns. The following table gives these values, with some of those for mercury corrected and with those for vapour of carbonic anhydride added:—

* Phil. Mag. vol. xx. p. 526 (December 1885).

Values of $\dfrac{t}{p}\dfrac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ethyl bromide, C_2H_5Br.	Ether, $C_4H_{10}O$.	Chloroform, $CHCl_3$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	12·80	13·64	13·04	......	......	......	16·07	16·42	......
500	10·83	11·31	11·22	11·66	13·20	12·12	13·81	14·39	......
1000	10·10	10·37	10·51	10·85	11·89	11·20	12·95	13·83	......
3000	8·68	8·96	9·24	9·27	11·23	9·67	11·58	11·99	......
5000	8·22	8·26	8·66	8·46	9·73	......	10·89	11·29	......
10,000	......	......	......	......	......	......	10·03	10·39	7·62
15,000	.....	......	......	......	.....	......	9·50	9·89	7·63
20,000	......	......	......	......	.....	......	9·13	9·54	7·57
50,000	......	......	......	......	......	......	......	......	6·77

But now it may be pointed out that $\dfrac{t}{p}\dfrac{dp}{dt}$ is not a mere arbitrary expression for

$$\frac{t}{p}\frac{dp}{dt} = \frac{r}{A p u}$$

(Hirn, tom. i. p. 319). That is, it is the ratio between the total heat of evaporation and the heat expended in external work. What we have found, therefore, is that this ratio approaches constancy for widely different substances and under considerable differences of pressure. This approximation to constancy appears to me to lie at the basis of all the relations Messrs. Young and Ramsay have found.

The constancy of this ratio of internal and external work, for different vapours at one pressure, has been investigated by Messrs. Young and Ramsay from other data, but it does not seem to have occurred to them that it would be obtained in the simple way given above.

The author noticed that another relation, namely,

$$\frac{t^2}{p}\frac{dp}{dt},$$

gave values for each vapour, far more constant at different pressures than

$$\frac{t}{p}\frac{dp}{dt}.$$

The following table gives some of these values :—

Values of $\dfrac{t^2}{p}\dfrac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ether, $C_4H_{10}O$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	3426	3394	7053	......	5218	5049	......
500	3324	3329	7231	8437	4995	4909	......
1000	3313	3321	7247	8275	4932	4956	......
5000	3220	3233	......	7936	4745	4610	......
10,000	......	......	......	.....	4670	4528	1889
20,000	......	......	......	......	4570	4455	1991
50,000	......	......	......	......	......	......	2018

This suggested that probably an empirical relation of this kind could be found expressing the relation of pressure and temperature very simply and with considerable accuracy. Let, for instance, for steam the values of $\dfrac{t^{2\cdot25}}{p}\dfrac{dp}{dt}$ be formed. We get:—

t.	p.	$\dfrac{t^{2\cdot25}}{p}\dfrac{dp}{dt}$.
273	4·60	21660
298	23·55	21970
323	91·98	22020
348	288·5	21940
373	760·0	21870
398	1743·9	21830
423	3581·2	21790
448	6717·4	21770
473	11689·0	21950

Where the greatest and least values differ from the mean by only 0·7 per cent. But the expression, the values of which have been found, is integrable. Putting $n+1$ for the index of t, we get for a general approximate relation between the pressure and temperature of vapours,

$$\log_e p = a - \frac{\beta}{t^n}. \qquad \ldots \ldots \ldots \quad (1)$$

From this are easily derived the following equations, in which for convenience the logarithms are common logarithms.

$$\log p = a - \frac{b}{t^n} \qquad \ldots \ldots \ldots \quad (2)$$

$$t = \left(\frac{b}{a - \log p}\right)^{\frac{1}{n}}. \quad \ldots \ldots \quad (2\,a)$$

$$\frac{1}{p}\frac{dp}{dt} = 2{\cdot}3025\,\frac{nb}{t^{n+1}}. \quad \ldots \ldots \quad (3)$$

$$= 2{\cdot}3025n\,\frac{(a - \log p)^{\frac{n+1}{n}}}{b^{\frac{1}{n}}}. \quad \ldots \quad (3\,a)$$

$$\frac{t}{p}\frac{dp}{dt} = 2{\cdot}3025\,\frac{nb}{t^{n}} \quad \ldots \ldots \quad (4)$$

$$= 2{\cdot}3025n(a - \log p). \quad \ldots \ldots \quad (4\,a)$$

For the latent heat, besides the ordinary formula,

$$\mathrm{L} = m - \frac{n}{(a - \log p)^{\frac{1}{n}}}. \quad \ldots \ldots \quad (5)$$

And consequently if v is the volume in cubic metres of the vapour and s that of the liquid,

$$v - s = \frac{\mathrm{JL}}{t\,\dfrac{dp}{dt}}$$

$$= \frac{13{\cdot}497\mathrm{L}}{pn(a - \log p)}. \quad \ldots \ldots \quad (6)$$

In all these equations the quantity required is expressed simply in terms of the pressure or the temperature, a result not obtainable with the formulæ previously used.

Formulæ for Steam.

To test the value of these equations, the author has calçulated the constants for steam most suitable for the complete range of Regnault's experiments, from -30° C. to 230° C., and from $0{\cdot}4$ millim. pressure to 20,000 millim. pressure. The proposal of a new empirical formula, and one not so accurate as Rankine's or Regnault's, for the relation of p and t in the case of steam, will probably appear the reverse of commendable. Still the fact that it gives a series of expressions, all directly derived from it, simple enough for ordinary use in engine calculations and accurate enough for practical purposes, is a strong reason in its favour. Its applicability can only be determined by testing its accuracy in a sufficient number of cases. In all the following calculations the calculated values are compared with the most accurate values thus far computed, over a range of pressure and temperature greater than would occur in practical cases.

The primary equation, derived from Regnault's data, for millimetres of mercury, Centigrade degrees reckoned from

$-273°$ C., and common logarithms is

$$\log p = 7\cdot5030 - \frac{7579}{t^{1\cdot25}}, \quad \ldots \quad \ldots \quad (7)$$

which gives

$$t = \left(\frac{7579}{7\cdot5030 - \log p}\right)^{\frac{4}{5}} \quad \ldots \quad \ldots \quad (7a)$$

The following table gives the values of p calculated from t with Regnault's experimental values and values calculated by Rankine's formula for comparison:—

Temperature, Centigrade.	Temperature, absolute.	Pressure in millims. Regnault.	Pressure in millims. by formula.	Error in millims.	Pressure in millims. by Rankine.	Error in millims.
$-3\overset{\circ}{0}$	$24\overset{\circ}{3}$	0·386	·401	+ ·015	·35	− ·036
−20	253	0·91	·982	+ ·072	·89	− ·02
−10	263	2·08	2·229	+ ·149	2·07	− ·01
0	273	4·60	4·709	+ ·109	4·47	− ·13
5	278	6·53	6·69	+ ·16		
10	283	9·17	9·40	+ ·23	9·05	− ·12
15	288	12·70	13·01	+ ·31		
20	293	17·39	17·83	+ ·44	17·33	− ·06
25	298	23·55	24·07	+ ·52		
30	303	31·55	32·18	+ ·63	31·57	+·02
35	308	41·83	42·61	+ ·78		
40	313	54·91	55·72	+ ·81	55·05	+·14
45	318	71·39	72·24	+ ·85		
50	323	91·98	92·85	+ ·87	92·26	+·28
55	328	117·48	118·30	+ ·82		
60	333	148·79	149·48	+ ·69	149·15	+·36
65	338	186·94	187·50	+ ·56		
70	343	233·08	233·61	+ ·53	233·48	+·40
75	348	288·50	288·60	+ ·10		
80	353	354·62	353·59	−1·03	355·04	+·42
85	358	433·00	433·21	+ ·21		
90	363	525·39	523·48	−1·91	525·70	+·31
95	368	633·69	633·72	+ ·03		
100	373	760·00	757·35	−2·65	760·0	0
105	378	906·41	904·27	−2·14		
110	383	1075·4	1071·5	−3·9	1074·8	− ·6
115	388	1269·4	1263·3	−6·1		
120	393	1491·3	1485·6	−5·7	1490·1	−1·2
125	398	1743·9	1735·4	−8·48		
130	403	2030·3	2020·2	−10·1	2028·0	−2·3
135	408	2353·7	2347·5	− 6·2		
140	413	2717·6	2710·2	− 7·4	2713·8	−3·8
145	418	3125·6	3114·6	−11·0		
150	423	3581·2	3564·5	−16·7	3575·5	−5·7
155	428	4088·6	4064·4	−24·2		
160	433	4651·6	4633·4	−18·2	4643·6	−8·0
165	438	5274·5	5262·6	−12·9		
170	443	5961·7	5941·6	−20·1	5951·2	−10·5
175	448	6717·4	6694·2	−23·2		
200	473	11689·0	11665·4	−23·6	11675·0	−14·0
230	503	20926·0	20951·7	+25·7	20945·0	+19·0

The following short table gives some values of t calculated from p :—

p.	t.	
	Calculated by (7a).	Observed.
4·60	272·7	273
91·98	322·8	323
760·00	373·2	373
3581·2	423·2	423
11689·0	473·1	473

The following are the derivative expressions. A few values are calculated from each and compared with the values very laboriously calculated by Zeuner from Regnault's formula.

$$\frac{1}{p}\frac{dp}{dt} = \frac{21815}{t^{2\cdot25}} \quad \cdots \cdots \quad (8)$$

$$= \frac{(7\cdot5030 - \log p)}{441\cdot3}. \quad \cdots \quad (8\,a)$$

t.	$\dfrac{1}{p}\dfrac{dp}{dt}$.	
	By formula (8).	From Zeuner.
273	·07201	·07150
323	·04932	·04979
373	·03567	·03577
423	·02688	·02685
473	·02090	·02083

$$\frac{t}{p}\frac{dp}{dt} = \frac{21815}{t^{1\cdot25}} \quad \cdots \cdots \quad (9)$$

$$= 2\cdot8782(7\cdot5030 - \log p). \quad (9\,a)$$

t.	p.	$\dfrac{t}{p}\dfrac{dp}{dt}$.		From Zeuner.
		By equation (9).	By equation (9 a).	
273	4·60	19·659	19·69	19·52
323	91·98	15·929	15·94	16·08
373	760·00	13·304	13·30	13·34
423	3581·2	11·368	11·37	11·36
473	11689·0	9·890	9·89	9·85

The latent heat of vaporization has hitherto been expressed only in terms of the temperature by the empirical formula

$$L = 796 \cdot 23 - 0 \cdot 695 t, \quad \ldots \ldots \quad (10)$$

where t is the absolute temperature, and the smaller terms containing higher powers of t are omitted. From the relation between p and t we get

$$L = 799 - \frac{894}{(a - \log p)^{\frac{2}{3}}}. \quad \ldots \ldots \quad (10\,a)$$

		L.		From Zeuner.
t.	p.	By equation (10).	By equation (10a).	
273	4·60	606·5	607·0	606·5
323	91·98	571·8	571·7	571·7
373	760·00	537·0	536·3	536·5
423	3581·2	502·3	501·0	500·8
473	11689·0	466·5	465·9	464·3

The new formula (10 a) is more accurate than the one (10) commonly used.

Let v be the volume in cubic metres of a kilogram of steam, and s the volume of the same quantity of water, usually taken at 0·001,

$$v - s = 10 \cdot 821 \frac{L}{p(a - \log p)}, \quad \ldots \ldots \quad (11)$$

where p is still expressed in millimetres.

	v — s.	
p.	By equation (11).	From Zeuner.
4·60	208·7	210·6
91·98	12·14	12·05
760·00	1·652	1·650
3581·2	·3833	·3839
11689·0	·1255	·1257

Other Vapours.

The following equations may be useful. That for ether agrees extremely well. The mercury equation less well; but the errors are considerably less than those of Rankine's equation in his paper of 1850. The data are all from Regnault.

Z 2

Alcohol :—

$$\log p = 7{\cdot}448 - \frac{8784}{t^{1{\cdot}29}}.$$

Ether :—

$$\log p = 6{\cdot}9968 - \frac{3047}{t^{1{\cdot}153}}$$

Mercury :—

$$\log p = 9{\cdot}8651 - \frac{597{\cdot}5}{t^{0{\cdot}69}}.$$

Carbonic acid :—

$$\log p = 8{\cdot}4625 - \frac{302{\cdot}8}{t^{0{\cdot}77}}.$$

XLIII. *The Law of Error and the Elimination of Chance. By*
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College, London.*[*]

ONE of the principal uses of the Law of Error is to elimi-
nate chance in cases like the following.   The mean (or
sum) of a set of observations[†] differs by a certain extent
from an assigned value[‡] ; usually that value which, upon
the supposition that no disturbing cause other than chance
had been at work, would be most likely to occur.   It is
required to determine the probability that the observed
divergence is due to a disturbing cause rather than mere
chance.   The general method may be summarized as follows.
Let x be the extent of observed divergence from the value
most probable on the supposition of mere chance.   The pro-
bability of this amount of divergence in an assigned direction
(positive or negative) occurring by mere chance is approxi-
mately

$$\int_{x}^{\infty} \frac{1}{\sqrt{\pi}\,c}\, e^{-\frac{x^2}{c^2}}\, dx,$$

where c is a constant depending upon the number and cha-
racter of the observations.   To which is to be added a certain
term outside the sign of integration, when we are dealing with
discrete errors, as in Bernouilli's theorem, rather than with
continuous quantity, as in the ordinary theory of errors of

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[*] Communicated by the Author.
 [†] Or more generally *elements* subject to definite laws of facility ; such
as those which Mr. Galton supposes to obey individually the simplest
binomial law, and by their composition to constitute an approximate
probability-curve, such as we find *in rerum naturâ* (Phil. Mag. Jan. 1875).
 [‡] Whether a fixed quantity or the mean (or sum) of another set of
observations (or more generally *elements*).