LXV. On the isopiestic temperatures of saturated vapours of different substances

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To cite this article: Alfred W. Porter B.Sc. (1907) LXV. On the isopiestic temperatures of saturated vapours of different substances , Philosophical Magazine Series 6, 13:78, 724-726, DOI: [10.1080/14786440709463652](https://doi.org/10.1080/14786440709463652)

To link to this article: <http://dx.doi.org/10.1080/14786440709463652>

Published online: 16 Apr 2009.

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being used as ordinates and the corresponding inversion temperatures t_i as abscissæ. The curve thus represents the relation connecting the inversion temperature of the gas under consideration with its initial pressure. The curves fully confirm the conclusion of Witkowski and Porter that the inversion temperature is a function of the pressure. The values of the inversion temperature for air calculated by Witkowski by the aid of the empirical formula given by Rose-Innes ($+360^\circ$), and by means of that of van der Waals ($+500^\circ$) are, it is true, somewhat high when compared with those obtained by myself; but it must be remembered that the second value ($+500^\circ$) was calculated on the assumption of a small pressure-difference (1 atmo.), whereas my figures refer to the integral value of the Joule-Kelvin effect when a gas expands from a high pressure to 1 atmo.

In conclusion, I would refer to the connexion which appears to exist between the shape of the curve for air and the behaviour of this gas in a liquefying apparatus. By means of the apparatus described by me in 1902*, which I am in the habit of using at lectures for the demonstration of the liquefaction of air, it is easy to show that liquefaction takes place only so long as the initial pressure does not fall below 80 atmos.; a further expansion from pressures which are below 80 atmos. is entirely without result. From the accompanying figure it is seen that precisely at the point corresponding to a pressure of 80 atmos. the curve takes a sharp bend, and that at this point a sudden drop takes place in the temperature of inversion, whereby also the cooling effect rapidly decreases, the behaviour of air beyond this point approaching in this respect more and more nearly that of hydrogen, whose inversion temperature is very low.

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LXV. *On the Isopiestic Temperatures of Saturated Vapours of Different Substances.* By ALFRED W. PORTER, *B.Sc.*, *Fellow of, and Assistant Professor of Physics in, University College, London* †.

IN the *Philosophical Magazine* for Jan. 1886 Ramsay and Young published a law (known by their names) connecting the temperatures at which different saturated vapours have the same vapour-pressure. The law has been employed in two somewhat different forms. One only of these forms

* K. Olszewski, *Bull. Acad. Crac.* 1902, p. 623.

† Communicated by the Author.

is consistent with a general relation connecting vapour-pressure and temperature. This form only will be referred to here, and it may be stated thus:—

If T and T_0 be the temperatures at which two substances have the same vapour-pressure, and T' , T_0' be two temperatures at which the same substances have another value of pressure the same for both, then

$$\frac{T_0}{T} - \frac{T_0'}{T'} = c(T_0 - T_0'), \text{ where } c \text{ is a constant.} \quad (1)$$

Hence if $\frac{T_0}{T}$ be plotted against T_0 a straight line will be obtained.

In the Phil. Mag. for September 1902 (p. 337) the late Prof. J. D. Everett subjects this law to the criticism that it is equivalent to neglecting the term $\frac{\gamma}{T^2}$ in Rankine's vapour-pressure equation

$$\log p = \alpha - \frac{\beta}{T} - \frac{\gamma}{T^2}.$$

This is shown by writing equation (1) in a form equivalent to

$$\frac{b}{T} - \frac{b_0}{T_0} = 1,$$

and then pointing out that Rankine's shortened formula leads to this equation: for the shortened formula gives

$$\log p = \alpha - \frac{\beta}{T} = \alpha_0 - \frac{\beta_0}{T_0},$$

whence

$$\frac{\beta}{T} - \frac{\beta_0}{T_0} = \alpha - \alpha_0.$$

It would seem, however, that the criticism that the law will hold only when squares of the reciprocal temperatures can be neglected, is not justifiable; for it rests on the assumption that we are restricted to Rankine's form of equation.

In order that Ramsay and Young's law shall be accurately true, all that is necessary is that

$$f(p) = A - \frac{B}{T},$$

where the left-hand side may be any function of the pressure which is identical for the substances in question.

Now in his Treatise on Thermodynamics Bertrand showed that the equation

$$p = G \left(\frac{T - a}{T} \right)^n; \quad \text{or} \quad p^{\frac{1}{n}} = g \left(1 - \frac{a}{T} \right)$$

is a very accurate expression for representing the vapour-pressures of most substances. In the case of water vapour the best values of the constants are

$$n = 42.855 \quad \text{and} \quad a = 88.2;$$

the error in the temperature corresponding to any given pressure is less than .3° C. for all temperatures between -30° C. and +230° C. A formula with only .5° C. temperature error is obtained by taking $n = 50$ and $a = 78.3$, and this value of n gives practically the same accuracy for numerous other substances tested.

Such a formula is not as accurate as Rankine's complete formula, but it is much more so than the shortened formula as the following table shows. In column 3 are shown values of the pressure of water vapour calculated from the formula $\log_{10} p = 8.49375 - \frac{2093.6}{T}$; in column 4 the differences from Regnault's experimental values; while columns 5 and 6 contain similar values for Bertrand's formula ($n = 50$).

T.	p observed.	Rankine's Formula.		Bertrand.	
		p calculated.	Δ_R .	Calculated.	Δ_B .
273	4.6	6.7	+ 2.1	4.54	- .06
323	91.98	102.7	+10.7	93.07	+1.09
373	760	760	0	760	0
433	4651.60	4556	- 95.6	4633.55	- 18
473	11689	11682	- 7	11682.84	- 6
503	20926.4	21454	+528	21036.00	+110

Now Bertrand's formula carries with it the complete accuracy of Ramsay and Young's Law, for it is of the general form mentioned above. Since, moreover, it is far more accurate than Rankine's shortened formula, it follows that the Ramsay and Young law is also in general more accurate than Professor Everett's criticism would seem to imply.