Note on a "Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids."

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Hence the equation to a meridian m degrees from the central meridian is

$$\frac{x}{a} = m \cos \left(\frac{y}{a} \cdot 1^\circ \right).$$

V. *Note on a "Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids."* By T. E. THORPE, Ph.D., F.R.S., and A. W. RÜCKER, M.A., F.R.S.*

A PAPER bearing the above title was published by us in the Journal of the Chemical Society of London for April 1884, and has recently been discussed by MM. A. Bartoli and E. Stracciati†. As these gentlemen have done us the honour to make use of a formula deduced by us from the simple expression given by Mendelejeff for the expansion of liquids, we should like to state exactly the position which we ourselves think ought to be assigned to it, and the use which may legitimately be made of it.

Prof. Mendelejeff has shown‡ that the expansion of liquids under constant pressure between 0° C. and their boiling-points may be expressed by means of the very simple formula

$$V_t = \frac{1}{1 - kt};$$

where V_t is the volume at t° (that at 0° C. being unity), and k is a quantity which differs for different substances, but which may for any one substance be considered invariable between 0° C. and the neighbourhood of the boiling-point.

The great merit of Mendelejeff's law is that it is proved by him to express the law of expansion to within the limits of the differences between the results of different observers experimenting on the same liquid. Thus, if the results of any one observer alone are considered, they may no doubt be most

* Read April 10, 1886.

† *Ann. Chim. Phys.* Mars 1886, p. 384.

‡ *Journ. Chem. Soc.* April 1884.

accurately expressed by a formula of the type

$$V_t = 1 + a't + b't^2 + c't^3.$$

Another equally reliable observer will, however, obtain for the same liquid a formula

$$V_t = 1 + a''t + b''t^2 + c''t^3,$$

where a' , b' , c' differ appreciably from a'' , b'' , c'' . These slight differences depend on the unavoidable errors of experiment, which may perhaps in the future be diminished, but which at present affect the work of the best observers using the best known methods. Hence formulæ such as those given above can only be considered as approximations to the true law of the expansion of the liquid to which they refer. That law will be most nearly given by combining the results of several physicists whose methods and observations are equally good, rather than of relying upon those of any one.

Now Mendelejeff has shown that the volumes calculated at different temperatures by means of the formula

$$V_t = \frac{1}{1 - kt}$$

differ less from the results of good observers than they do from one another. It might in any given case be possible to obtain another more complex formula which would express the *mean result* more accurately, but it would remain very doubtful whether the greater mathematical accuracy obtained represented the physical facts more closely. Mendelejeff (as we think rightly) considers that the simplicity of the formula which he has suggested gives it a special claim upon our attention; and he proves that it expresses, at all events as a first but very close approximation, all *that we certainly know* about the expansion of liquids.

It is therefore no argument against Mendelejeff's formula to remark, as MM. Bartoli and Stracciati have done, that

$$V_t = \frac{1}{1 - kt} = 1 + kt + k^2t^2 + k^3t^3 + \&c.;$$

and that in the formulæ given by Pierre, Kopp, Hirn, Thorpe,

&c., the constants a , b , and c do not differ by a constant ratio, as the expression would require. This criticism would only hold good if all these observers had obtained the same, or closely identical, values of a , b , and c ; whereas, as a matter of fact, the values of b and c given by different observers may differ very widely. The very merit of Mendelejeff's remark is that, although the results of no one physicist are expressed by

$$V_t = 1 + kt + k^2t^2 + k^3t^3,$$

yet that this formula in its simpler form,

$$V_t = \frac{1}{1 - kt},$$

expresses the results of all as accurately as those results will allow; and that since it is thus sufficiently accurate and extraordinarily simple, it may claim to be the best general formula hitherto proposed for expressing the laws of liquid expansion.

These remarks are subject to the conditions which Mendelejeff made clear, that the formula was only applied to the range of temperature between 0° and the neighbourhood of the boiling-point, and that the constant k increases slightly as the temperature rises. This latter fact indicates that the law, though very accurately expressing the known facts, is only an approximation to the truth.

Mendelejeff's formula, then, appears to us to stand in somewhat the same position as Boyle's or Charles's laws. It is a first approximation, which expresses the facts, under given conditions of temperature and pressure, with great accuracy. The difference between the two cases is that, whereas the deviation of each of the principal gases from Boyle's law has been studied, Mendelejeff has shown that the most careful researches do not enable us to state with certainty what is the magnitude of the error caused by applying his formula to any particular liquid. They show only that k increases very slightly as the temperature rises.

Having thus defined as accurately as we can the position which we think that Mendelejeff's law holds, we need hardly say that we do not claim any higher status for our own formula connecting the law of expansion and the critical temperature.

We were most careful to express in our paper our appreciation of the fact that our expression was based upon Mendelejeff's, and therefore it ranked only as a theoretical deduction from an extremely close approximation to the truth, and is to be employed only under the conditions for which that approximation was valid.

Thus we have shown that the critical temperature of a liquid (T_c) is given very approximately by the formula

$$T_c = \frac{TV - 273}{a(V_t - 1)};$$

where V_t is the volume at t° C., $T = 273 + t$, and a is a constant which we proved is nearly $= 2$.

We should, however, never have thought of applying this formula to determine the critical temperature of water from the expansion up to 200° C. We have not applied it to water at all, on account of the well-known peculiarities of the expansion of that substance; but had we done so, we should have regarded it as holding only between 0° C. and the boiling-point. We have distinctly laid it down that it is under these conditions k is to be determined*. In proving, therefore, that the values of the critical temperature, calculated from the expansions at temperatures above the boiling-point, vary very widely from those obtained under the conditions adopted by Mendelejeff and ourselves, MM. Bartoli and Stracciati have only shown that the formula does not hold good under circumstances to which its authors never intended it to be applied.

We are, however, gratified to find that these gentlemen, notwithstanding their criticisms, show a reliance upon our formula even greater than that which we feel ourselves. The values of the constant a given in our paper prove that its true value is uncertain, at all events to 1 per cent. or more. MM. Bartoli and Stracciati, however, give in their second paper a number of critical temperatures calculated by the formula to tenths of a degree. If the tenth of a degree is to be determined with accuracy, the constant a must be known to 0.025 per cent.

* Journ. Chem. Soc. *loc. cit.* p. 139.