

RELATIONS BETWEEN CRITICAL TEMPERATURES, BOILING-POINTS, AND EXPANSION COEFFICIENTS OF LIQUIDS. FORMULA OF AVENARIUS.

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A recent note on this subject by E. B. R. Prideaux* induces me to offer two remarks; they will, I think, be found useful for this kind of research.

I.

The formula of Mendelejeff †—

$$k = \frac{V_2 - V_1}{V_2 T_2 - V_1 T_1}, \dots \dots \dots (1)$$

as well as the formula of Thorpe and Rücker, ‡ which follows from it—

$$T_k = \frac{T_2 D_1 - T_1 D_2}{A(D_1 - D_2)}, \dots \dots \dots (2)$$

are certainly very interesting and admit of being applied in such researches.

It should never be overlooked, however, that these relations are merely approximations. In fact, the formula of Mendelejeff may also be written—

$$V_t = \frac{V_0}{1 - kt} = V_0(1 + kt + k^2 t^2 + k^3 t^3 \dots).$$

Thus developed into a series, the expression $1/(1 - kt)$ only forms a special case of the usual empirical formula—

$$V_t = V_0(1 + at + bt^2 + ct^3 \dots),$$

but it offers less scope for determining the values and the signs of the coefficients of the terms containing t ; it can, therefore, only give a smaller exactness.

It is, moreover, easy to convince ourselves that when we calculate k for the same liquid, starting from diverse systems of values V_1, V_2, T_1, T_2 , the discrepancies will certainly much exceed the errors of observation.

In accord with the theory experiments thus confirm that the relation (1) can only be approximately true; it will in general be the more accurate, the less the dilatation of the liquid will deviate from the linear form.

Somewhat the same statement may be made with regard to relation (2), which—as is well known—results from a combination of formula (1) with a consequence of the theory of corresponding states.

Relation (2), however, or its equivalent—

$$\frac{V_1}{V_2} = \frac{D_2}{D_1} = \frac{aT_c - T_2}{aT_c - T_1} \dots \dots \dots (3)$$

* Prideaux, *Trans. Faraday Soc.* **6**, 155 (1911).

† Mendelejeff, *Z. Chem. Soc. Trans.* **45**, 126 (1884).

‡ Thorpe and Rücker, *ibid.*

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expresses the dilatation of liquids much better than (1), as Thorpe and Rücker pointed out. Nevertheless, the approximate character of this relation results from the fact that, when we determine, for the same liquid, several values of a , these values will show discrepancies which will be much greater than the experimental errors.

We proved many years ago already* that the boiling-point on the absolute scale T_b may be substituted for the critical temperature T_c on the absolute scale. Thus we can write—

$$\frac{V_1}{V_2} = \frac{D_2}{D_1} = \frac{a'T_c - T_2}{a'T_c - T_1} \dots \dots \dots (4)$$

in which a' is a new constant approximately equal 3.09 (whilst $a = 1.974$ on average).

Thus we obtain an expression which will, on the whole, well represent the dilatation of liquids in large temperature intervals; particularly when the mean value of a is determined which best conforms to each liquid. Then the calculated and observed densities will very rarely differ by more than 1 : 1,000.

It will be noticed that formula (4) follows from formula (3) by having recourse to the relation—

$$\frac{T_c}{T_b} = 1.55$$

which I derived,† in quite an independent manner, at the same time as Guldberg in 1890.

II.

It would be of considerable advantage to use other, more accurate formulæ, instead of those just discussed, which are at present largely applied in the study of the relations between the expansion and the volatility of liquids. This is all the more advisable, since we possess, in the formula of Avenarius, already a relation which is more exact than those mentioned, as Mallet and Friderich demonstrated in 1902.‡ As this memoir was published in Proceedings, which are not readily accessible in chemical laboratories, I thought it would be appropriate if I called attention to the principal results of this investigation.

The formula of Avenarius—

$$\log V = c - d \log (A - t) \dots \dots \dots (5)$$

contains only three constants; how they are calculated has been indicated by the just quoted authors. Verified by the data concerning the orthobaric densities of 25 normal non-associated liquids studied by S. Young, the formula expresses very accurately the orthobaric expansion curve up to temperatures about 30° or 40° below the critical temperature. Within these limits the formula yields excellent results for temperature intervals ranging from 150°

* Guye and Jordan, *Bull. Soc. Chim.* **15**, 306 (1896).

† Guye, *Bull. Soc. Chim.* **4**, 262 (1890); a preliminary note had been communicated to the meeting of the Paris Société Chimique of July 4, 1890 (*loc. cit.* p. 104). Guldberg published his memoir in the *Zeits. Physik. Chem.* **5**, 374. The mean value for $T_c/T_b = 1.55$, at which I had arrived, viz., $T_c/T_b = 1/1.55 = 0.65$, is in agreement with that indicated by Guldberg, viz., 0.67. I give these details because the relation is generally associated only with the name of Guldberg.

‡ Mallet and Friderich, *Arch. Sc. phys. nat. Genève*, **14**, 50 (1902).

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to 300°. The formula permits of determining, by a very simple calculation, for each temperature the value dv/dt —

$$\frac{dv}{dt} = \frac{d \log e}{A - t} \dots \dots \dots (6)$$

and consequently also the dilatation coefficient $\frac{1}{v} \frac{dv}{dt}$ at any temperature.

The observed and calculated values of dv/dt are in remarkable concordance.

Very interesting approximate relations now exist between the three constants of formula (5), namely: (1) the constant A is very nearly the observed critical temperature, exceeding the latter generally by 5° or 10°. (2) There is a sensibly constant interrelation between the constants c and d ; as a first approximation $c : d$ is = 3.78. In the case of the 25 liquids studied by Mallet and Friderich, the difference between the ratio $c : d$ and the figure 3.78 amounts in the mean to ± 1 per cent. It is remarkable that the number 3.78 agrees almost exactly with that found by S. Young for the ratio of the observed critical density to the theoretical critical density.

These results are particularly interesting. According to the first we may ask ourselves, in conjunction with several authors, whether the critical observed temperatures correspond to the theoretical considerations which concern the liquid state. The second, combined with the first, shows that the formula of Avenarius contains, as a first approximation, not any specific constant of the liquid state: A coincides within a few degrees with the critical temperature; the term c must represent the critical density, and the ratio $c : d$ is constant.

It will finally be noticed, as the authors have pointed out, that the formula of Avenarius must necessarily be more precise than those of Mendelejeff and of Thorpe and Rücker. The expression (6) may indeed be written—

$$\frac{dv}{dt} = \frac{\frac{d}{A} \log e}{1 - \frac{t}{A}},$$

which is evidently analogous to the formula—

$$v_t = \frac{v_0}{1 - kt}$$

of Mendelejeff. The formula of Avenarius therefore expresses the coefficient $\frac{dv}{dt}$ by a function which is identical with that selected by Mendelejeff for representing the volume, and must thus always be superior to it.

All these considerations will certainly justify a more frequent application of this formula.

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