[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 153.]

SOME NEW FORMULAE CORRELATING THE VARIOUS CONSTANTS FOR NON-ASSOCIATED LIQUIDS.[1]

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Received February 14, 1908.

It was shown by W. G. Kistiakovski[2] that the relation $\frac{AM}{T} = K_k$ holds for a large number of substances where M = molecular weight in liquid state, A = capillary constant (rise in a capillary tube of unit radius), and T = absolute boiling point, the value of K varying from 1.04 to 1.17.

It has been shown[3] that the drop weight of non-associated substances is proportional to the surface tension, hence by the equations $\gamma = \frac{1}{2} g r h d$ and $w = v d$ it is obvious that by substituting v in the Kistiakovski relation we should obtain a constant similar to that obtained from the capillary constant provided the volume be that delivered from unit tip. Since we have insufficient data to enable us to calculate the magnitude of v under these conditions we must employ the drop volume obtained in a previous paper.[3] This will not affect the constancy of the relation but will simply lead to a new empirical constant,

$$\frac{vM}{T} = K.$$

Solving for the extrapolated values for drop volume we get:

TABLE I.

Substance.	K.
Benzene	67.4
Pyridine	67.3
Chlorbenzene	68.4
Aniline	67.6
Quinoline	68.8

This shows that the statement is as generally justifiable for drop volume as for capillary rise despite the extrapolation in the first case since drop volumes have not been estimated up to the boiling point. In any subsequent use of drop volume determination as a method for obtaining molecular weights, it would be advantageous if such a formula as the above could be shown to be general at temperatures other than the boiling point, since the molecular weight of a non-associated substance could then be calculated from a single estimation at a temperature which would introduce no extra experimental difficulties. The most probable direc-

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[1] Extract from the author's dissertation.

[2] *Elektrochem.* (8) 376, 1902 and (12) 513, 615, 1906.

[3] Previous article in this journal.

tion for the formula to take is that of "corresponding states" shown to be at least approximately true by the following results:

TABLE II.

Substance.	Mean specific temperature coefficient of drop volumes.		Mean molecular coefficient.
Benzene	0.0000	13315	0.0104
Pyridine	....	12669	0.0100
Chlorbenzene	....	09605	0.0108
Quinoline	....	0.717	0.0103
Aniline	....	11175	0.0104
Carbon tetrachloride	....	06946	0.0107
			0.01043 ± 4%

An agreement closer than that of *k* (Ramsay and Shields) by the capillary rise method and derived direct from experimental results not from a smoothed curve. It thus seems probable that the formula

$$\frac{Mv}{T} = K_{(B. P.—T.)}$$

will be found to hold at all corresponding temperatures where M = molecular weight, v = drop volume, and T = absolute temperature of observation. $K_{(B. P.—T.)}$ = constant for the particular state, *i. e.*, for the difference between the temperature of estimation and the boiling point. Solving the equation for the experimental values[3] formerly obtained, we obtain by extrapolation the numbers shown in Table III.

TABLE III.

Substance.	Values of K for temperatures below the boiling point of: 0	10	20	30	40	50	60	70	80	90	100
Benzene	6736	7232	7763	8321	8925	9553	10200	10960	..	..	..
Pyridine	6727	7178	7640	8141	8493	9213	9808	10430	1110	1180	1256
Aniline	6765	7159	7575	8007	8460	8936	9437	9969	1052	1111	1173
Chlorbenzene	6844	7302	7777	8284	8807	9365	9963	10580	1124	1185	1270
Quinoline	..	..	..	8593	9006	9413	9914	10390	1090	1139	1198
	6768	7218	7689	8269	8738	9296	9864	1046	1094	1154	1224

The agreement is very good, considering that the values are nearly all from extrapolated drop volumes, some, as with aniline and quinoline, over more than 100°. The deviations from the average are apparently no function of the molecular weight or boiling point and are consequently probably due largely to errors of extrapolation. The generalization is, however, likely only to be accurate at temperatures not too far removed from the boiling point as evidenced by the increase of percentage variation in the values for K as we retreat from the boiling point and by the fact that if it held rigidly very far above the boiling point it would force the conclusion that the critical temperature of all non-associated substances lies at the same distance from their boiling point, a conclusion contrary to fact.

Further work may make it possible to correct the formula much as Trouton's law has been modified by Nernst, but for the present approximate accuracy only is attainable. It now remains to show what may be derived from the formula in its present state.

(1) Use of the formula to derive molecular weight from a single drop volume determination, $M = \frac{K_{(\text{B. P.}-\text{T})}T}{v}$.

The values used for K are those obtained by averaging the numbers shown in Table III, eliminating the values for quinoline and aniline at temperatures less than 80° from the boiling point so that all experimental values for K are extrapolated over the same range.

The drop volumes used are those directly obtained, no attempt being made at mutual correction, so that the values are such as would be obtained from isolated determinations.

TABLE IV.

Substance.	Boiling pt.	Molecular wt.	Calculated molecular wt. from expts. over range of 10° to 60°.
Chlorbenzene	132	112.4	111.8–112.2
Pyridine	114.5	78.0	79.0– 80.0
Aniline	183.5	93.0	100.0–101.0
Benzene	80.4	79.0	79.0– 80.0

This gives from estimations burdened with ordinary experimental error as close agreement as necessary for practical work in the laboratory, even assuming the average values of K used to be accurate, which is scarcely probable. The formula has thus sufficient accuracy in its present form for use in the organic laboratory.

If $\frac{Mv}{T} = K_{(\text{B. P.}-\text{T.})}$ is generally true in the neighborhood of the boiling point, it follows that

$$v = \frac{K_{(\text{B. P.}-\text{T.})}T}{M} \text{ and } \gamma = \frac{TK_{(\text{B. P.}-\text{T.})}}{M}d,$$

hence if the molecular weight of a substance be known the value of the drop volume can be calculated by use of the various values of $K_{(\text{B. P.}-\text{T.})}$ and by using the corresponding value for density we can write the formula of Ramsay and Shields:

$$\frac{K_{(\text{B. P.}-\text{T.})}T}{M}d\left(\frac{M}{d}\right)^{2/3} = k_{\text{temp.}}(\tau - 6),$$

and thus calculate the critical temperature as shown in Table V.

TABLE V.

Substance.	Mol. wt.	Boil. pt.	Critical temp. from $K_{(B.P.-20)}$–766.	Average critical temp. from $K_{B.P.}$ to $K_{B.P.-40}$.	Mean experimental values.
*Chloroform	119.4	61.2	262.4	263.0	260±
Chlorbenzene	112.4	132.0	356.5	359.1	360±
*Ethylidene chloride	98.9	59.2	255.7	256.0	255±
*Toluene	92.0	111.0	320.1	320.6	321±
Pyridine	79.0	114.5	347.75	348.3	345±

The density data for the 3 substances marked * were obtained from smoothed curves from values published in Beilstein and elsewhere.

The agreement is good, especially that obtained by averaging the values over a series of K's indicating the error largely to lie in their insufficient definition. It is also interesting to note that ethylidene chloride, toluene and chloroform give correct results using as $k_{\text{temp.}}$ the value established as constant in previous work with other substances, *viz.*, 2.5694.[2]

Expressed in formula form these results become

$$\text{(1)} \qquad \text{M} = \frac{\text{TK}_{(\text{B. P.}-\text{T.})}}{v} \text{ or } v = \frac{\text{TK}_{(\text{B. P.}-\text{T.})}}{\text{M}}.$$

$$\text{(2)} \qquad vd\left(\frac{\text{K}_{(\text{B. P.}-\text{T.})}\text{T}}{vd}\right)^{2/3} = k_{\text{temp.}}(\bar{\tau}-6) = (vd)^{1/3}(\text{K}_{(\text{B. P.}-\text{T.})}\text{T})^{2/3}.$$

$$\text{(3)} \qquad \frac{\text{K}_{(\text{B. P.}-\text{T.})}\text{T}d}{\text{M}}\left(\frac{\text{M}}{d}\right)^{2/3} = k_{\text{temp.}}(\tau-6) = \text{K}_{(\text{B. P.}-\text{T.})}\text{T}\left(\frac{d}{\text{M}}\right)^{1/3}.$$

Where $\left.\begin{array}{l} v = \text{drop volume} \\ d = \text{density} \end{array}\right\}$ at temperature T (absolute). M = molecular wt. τ = critical temp. — T. $\text{K}_{(\text{B. P.}-\text{T.})}$ constant for condition at boiling point — T degrees below boiling point.

Since it has been shown that the critical temperature of a substance can be calculated from a knowledge of its boiling point, molecular weight and a single density with an accuracy equal to that obtainable by direct experimental determination, it follows that we might by substitution of such a derived critical constant in the Nernst[2] modification of Van der Waals's[1] equation, using the boiling point as the specific state, solve for the critical pressure:

$$\log\frac{\pi}{p} = 1.75\log\frac{\text{T}_c}{\text{T}} + \alpha'\left[\left(\frac{\text{T}_c}{\text{T}} - 1\right) - \frac{1}{2.36}\left(1 - \frac{\text{T}}{\text{T}_c}\right)\right],$$

p thus becoming unity and T the boiling point of the substance, T_c being the critical temperature solved by equation 3. π being thus obtained, substitution of any other value for T in Nernst's equation leads to the evaluation of p (the vapor pressure) at any temperature.

With π (critical pressure) and T_c thus obtained the values of "a"

and "b" in Van der Waals's[1] gas equation are determinable

$$a = \frac{27}{(74)(273)^2}\frac{T_c^2}{\pi}$$

$$b = \frac{1}{(8)(273)}\frac{T_c}{\pi}$$

and still again knowing the value of π and p we may obtain the latent heat of vaporization from Nernst's[2] modification of Trouton's law.

$$\frac{\lambda}{1-\frac{p}{\pi}} = R\frac{T_1T_2}{T_1-T_2}\,ln\,\frac{p_1}{p_2}.$$

Summing up, therefore, we find that for a number of unassociated liquids:

(a) From a knowledge of the boiling point of the liquid and its molecular weight and a density we can by use of drop volume constants determine with very fair approximation:

(1) The surface tension (in terms of drop weight).
(2) The critical temperature and pressure, and hence
(3) The vapor pressure at any temperature.
(4) The latent heat of evaporation.
(5) The value of "a" and "b" in the Van der Waals's equation for the particular substance.

(b) From a drop weight determination by the same constants and a knowledge of the boiling point we can calculate the molecular weight of a substance and hence all the values under (a).

As to how far the equations in an unmodified form are absolutely general, sufficient data have not as yet been accumulated to show, nor have the values of K been defined with sufficient accuracy.

Further work will be published shortly upon this subject and on formulae and relations derivable from it, the present paper being more in the nature of a note than any attempt at a full treatment.

With approximate accuracy the values for K are:

$K_{(B.P.)} = 660$; $K_{(B.P.-20)} = 766$; $K_{(B.P.-40)} = 880$; $K_{(B.P.-10)} = 713$; $K_{(B.P.-30)} = 824$: $k_{\text{temp.})} = 2.5694$.

LABORATORY OF PHYSICAL CHEMISTRY,
NEW YORK CITY, N. Y.,
April, 1908.

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[1] Van der Waals's *Die Continuitat des gasformigen und flussigen Zustandes*, pp. 166–167. "Ist der Radius der Attraction bei allen Körpern gleich gross, so muss Capillaritätsconstante fur die verschiedenen Körper dem kritischen Druck proportional sein."

[2] *Nachrichten Kgl. Ges. Wiss. Göttingen*, 1906.

[2] E. C. Bingham, THIS JOURNAL, **28**, 717.