

Karl P. Link has kindly informed us that he and Mr. R. J. Dimler have measured the rotation of zinc L-lactate in the course of a research on some derivatives of lactic acid, soon to be published, and have found considerable variation in rotation with concentration. We have repeated and confirmed their measurements and, at their suggestion, now record the two sets of values over the wider range of concentrations from 1.5 to 7.0%. In this range the $[\alpha]_D$ values may be expressed approximately as $[\alpha]_D^{20} = -9.2^\circ + 0.4(c)$, in aqueous solution, for zinc L-lactate dihydrate. (The configuration of L-lactic acid is $\text{CH}_3-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{COOH}$.)

TABLE I
VARIATION OF ROTATION WITH CONCENTRATION, AQUEOUS SOLUTIONS OF ZINC L-LACTATE DIHYDRATE (ACCURACY $\pm 0.1^\circ$)

Concn. (as dihydrate)	$[\alpha]_D^{20}$ (Dimler and Link)	$[\alpha]_D^{20}$ (Maclay, Hann and Hudson)
1.5	-8.7°	-8.7°
3.0	-7.9	-7.9
4.0	-7.6	-7.5
5.0	-7.2	-7.1
7.0	-6.7	-6.6

In our article we expressed the opinion that the rotations $[\alpha]_D^{15} +6.84^\circ$ (*c*, 5.6) for zinc D-lactate dihydrate and $[\alpha]_D^{20} -6.83^\circ$ (*c*, 7.1) for zinc L-lactate dihydrate, found by Irvine,³ indicated some racemization of the lactic acids. It is now seen, however, that these values fit the new measurements very well, from which it may be concluded that the procedure which Irvine used in preparing the zinc lactates does not cause racemization and is therefore preferable to the more laborious procedure which we employed in order to exclude the possibility of racemization.

(3) Irvine, *J. Chem. Soc.*, 89, 935 (1906).

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Molecular Structure of Aliphatic Compounds and their Boiling Points

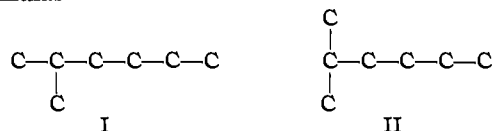
BY E. NEYMAN-PILAT

On the basis of Walker's formula C. R. Kinney recently¹ has developed a new system correlating molecular structure of organic compounds with their boiling points. In a paper dealing specially with aliphatic compounds, the boiling point numbers (b. p. n.) for carbon and hydrogen as well as

(1) C. R. Kinney, *THIS JOURNAL*, 60, 3032 (1938).

for some radicals and characteristic groups have been presented. From these data and the given formula the boiling points at atmospheric pressure of aliphatic compounds may be calculated easily and with fair accuracy.

C. R. Kinney has stated that due to the lack of adequate boiling point determinations recorded in the literature for the branched hydrocarbons, the b. p. n.'s for only the methyl, ethyl, propyl and butyl radicals were calculated and that even those may undergo some alteration when more boiling points will be recorded. This point of view would seem to be open to question, as some of the paraffin hydrocarbons listed in Table I of the quoted paper may be considered as being derivatives of different radicals. For example the 2-methylhexane may be treated as a methyl (I) as well as a butyl derivative (II) according to the structural formulas



In the same way the 3-methyloctane may be regarded as 2-pentylbutane and the 3-methylnonane as 2-hexylbutane, etc.

The calculated B. P. N. obviously must be independent of the way in which the structural formulas are expressed.

Taking as a basis the values of 0.8, 1.0 and 3.05 for C, H and CH_3 as given by Kinney, and calculating the B. P. N. for both formulas of each hydrocarbon, the characteristic values for the alkyl radicals have been established. The values as presented in Table I differ by 2.8 for all the neighboring members of the series, this being in accordance with the value calculated from Kinney's data for the CH_2 group. The calculated b. p. n.'s as seen from Table I are somewhat higher

TABLE I

Alkyl radical	B. p. n. calcd. by Kinney	B. p. n. calcd. by the author
CH_3	3.05	3.05
C_2H_5	5.5	5.85
C_3H_7	7.0	8.65
C_4H_9	9.7	11.45
C_5H_{11}		14.25
C_6H_{13}		17.05
C_7H_{15}		19.85
$\text{C}_{10}\text{H}_{21}$		28.25
$\text{C}_{15}\text{H}_{31}$		42.25

than those of Kinney but seem to be more accurate as may be seen from the following examples.

(1) The 2-methylhexane with a b. p. of 90° has the calcd. B. P. N. of 20.85. If expressed as 2-butylpropane its B. P. N. calcd. with the new value for the butyl radical 11.45 amounts to 20.85 and with the Kinney value 9.7 to 19.1. The b. p. calcd. from the last value amounts to 72.2° while from the first to 90.4° .

(2) For the 2-methylpentane b. p. 60° with the B. P. N. equal to 18.05, the corresponding values for the second formula 2-propylpropane are 18.05 when based on b. p. n. 8.65, and 16.4 when based on b. p. n. equal to 7.0 for the propyl radical. The corresponding calcd. b. p.'s are 60.7 and 41.7° .

(3) The 3,3-diethylpentane has the obsd. B. P. N. of 26.04, the calcd. by Kinney of 25.00 and the calcd. with the new increment for the ethyl radical (5.85) amounting to 25.70.

(4) The 2-methylheptadecane with a b. p. of $311^{\circ 2}$ has the B. P. N. equal to 51.65 ($13.6 + 35 + 3.05$ or regarded as 2-pentadecylpropane: $2.4 + 7 + 42.25$) and the calcd. b. p. of 314.1° .

Using for alkyl radicals the proposed values of b. p. n. the calculated boiling points are in better agreement with observed b. p. for all the ethyl derivatives quoted by Kinney. However, in the case of propyl derivatives as well as of 5-butyl-nonane, the Kinney values agree much better than those now proposed. It seems to be very plausible that these discrepancies are due either to inaccurate b. p. determinations or to some other unadditive factors bearing on the boiling phenomena.

Instead of calculating the b. p. n. for all the possible radicals, it seems to be much more advisable to calculate the B. P. N. of a compound as a sum of the atomic b. p. n. and take into account the number and kind of the branching present. The increment for a singular branching in the hydrocarbon series amounts in this system evidently to 0.75 ($3.8 - 3.05$) and must be subtracted from the total B. P. N. In such a way the B. P. N. for *e. g.*, the 2-ethylpentane (C_8H_{18}) will amount to: $(7 \times 0.8) + (16 \times 1) - 0.75 = 20.85$.

It is possible that the value of 0.75 which is true for a single branching, does not hold good in case of two radicals being attached to one carbon atom in the paraffinic chain, and that this is responsible for the discrepancies found in strongly packed molecules.

In addition to the above, mention should be

(2) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, New York, N. Y., 1939, p. 103.

made that Kinney in his calculations does not take into account the influence of the position of the radicals in relation to the whole molecule, although this considerably affects the boiling points of organic compounds.

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The Calculation of the Boiling Point Numbers of Aliphatic Compounds

BY CORLISS R. KINNEY

In Dr. Neyman-Pilat's note, "Molecular Structure of Aliphatic Compounds and their Boiling Points," the view was taken that, "The calculated B. P. N. obviously must be independent of the way in which the structural formulas are expressed." If this means that the B. P. N. (molecular boiling point number) of a compound may be calculated without regard for the relationships between the structural components in the molecule, the statement is misleading and the results obtained are variable and consequently of no value. This is true because the relationships between the atoms and groups in molecules do have an effect upon the boiling point of the substance.

By way of example, Dr. Neyman-Pilat suggested that the B. P. N. of 2-methylhexane may be calculated, considering it as 2-butylpropane, by adding the b. p. n. of the side chain butyl group to the b. p. n.'s for the propane chain. Since this gave erroneous results, a new set of b. p. n.'s for the alkyl radicals were proposed (Table I). However, these values were found by Dr. Neyman-Pilat to give unsatisfactory results for those derivatives in which the higher radicals were attached to a longer chain, which, of course, is of no advantage. Furthermore, these values must be used in a particular way, just as the original b. p. n.'s¹ must. This may be demonstrated as follows. Dr. Neyman-Pilat considered 2-methylhexane as 2-butylpropane and, by assigning a new b. p. n. to the butyl radical, obtained a satisfactory B. P. N. However, 2-methylhexane may also be considered as butyldimethylmethane and, if Dr. Neyman-Pilat's new value of 11.45 be used in calculating the B. P. N. of butyldimethylmethane, the result is 19.35 which is much too low. Therefore, by using Dr. Neyman-Pilat's values in a way in which they were

(1) Kinney, THIS JOURNAL, 60, 3032 (1938).