

(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

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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).

not designed to be used, just as erroneous results may be obtained as when the original b. p. n.'s are used in an erroneous fashion. Since these calculations also show that it is not possible to obtain universal b. p. n.'s for the alkyl groups as Dr. Neyman-Pilat has attempted, it seems advisable to retain the original values which were obtained on the basis that the alkyl radicals were derivatives of the normal paraffin hydrocarbons and not of the 2-methylparaffins. It is essential that the longest chain in the molecule be considered as the base to which the smallest possible radicals are attached. Following this procedure always gives uniform results. The underlying reason is well known to organic chemists in the fact that the boiling point of a substance is not only dependent upon the kind and number of atoms in the molecule, but is also dependent upon the arrangement of those atoms and especially upon the length of the chain.

Dr. Neyman-Pilat has suggested that a higher b. p. n. for the ethyl group than that given in the original paper would give better results. However, it should be pointed out that this is true particularly for the paraffin hydrocarbons and that the value was adopted because it gave more uniform results with all types of organic compounds.

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Parachor of Aluminum Bromide in Benzene

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The work described here was carried out with the object of determining if the molecular formula of aluminum bromide when dissolved in benzene is the same as that determined for molten aluminum bromide.¹ The method used was to determine the mean parachor of solutions of aluminum bromide in benzene, and to see whether an extrapolation (assuming that the parachor obeys the straight line mixture law) to 100% solute using the formula of Hammick and Andrew² would lead to a value of the parachor of pure aluminum bromide that agrees with the value determined by Sugden.¹

In this method

$$P_m = M_m \gamma^{1/4} / d$$

$$M_m = M_2(X) + M_1(1 - X)$$

(1) Sugden, *J. Chem. Soc.*, 320 (1929).

(2) Hammick and Andrew, *ibid.*, 754 (1929).

Before many measurements had been made, however, it was noticed that the solutions of aluminum bromide in benzene gradually separated into two layers: one, a dense light red oil which turned dark brown-purple on standing, and a less dense colorless layer. All our measurements were made before the separation into the second phase occurred. B. Menshutkin³ found that the presence of moisture or the introduction of hydrogen bromide into solutions of aluminum bromide in benzene caused the separation into two layers. In our work no hydrogen bromide had been introduced, so it is probable that some water vapor had reacted with the aluminum bromide in the benzene, liberating hydrogen bromide, which in turn caused the formation of the heavy oil. Norris and Rubinstein⁴ investigating the formation of complexes of aluminum bromide with toluene in the presence of hydrogen bromide, found by analysis that the complex was $Al_2Br_6 \cdot 6C_6H_5CH_3$. The oil in the case of benzene is probably $Al_2Br_6 \cdot 6C_6H_6$.

Because of the formation of this oil we were unable to carry on work in more concentrated solutions.

Experimental.—The benzene was allowed to stand for one week over mercury, fractionated three times, and dried over phosphorus pentoxide.

Bromine was purified by the method of P. C. Terwogt.⁵

Aluminum bromide was prepared by the method of Kaveler and Monroe.⁶ Samples were distilled directly into weighing vials in an atmosphere of dry carbon dioxide.

Densities were determined with a pycnometer with ground glass caps.

Surface tensions were determined using a slightly modified form of Sugden's apparatus.⁷ Successive readings were consistent to within 0.4%.

All measurements were made at $34.90 \pm 0.03^\circ$.

Table I lists the results obtained when the formula Al_2Br_6 is assumed.

Density of solution, d	Mole fraction Al_2Br_6 , X	Mean mol. wt., M_m	Surface tension, γ dyne/cm.	Mean parachor P_m
0.9454	0.01737	84.21	26.55	206.6
1.0035	.03330	93.21	27.07	211.9
1.0250	.04195	97.15	27.45	217.0
1.1070	.06345	106.95	27.64	221.5
1.1173	.08325	115.96	27.74	238.3
Extrapolated value of mean parachor when $X = 1.00$				470.4

When plotted, the mean parachors deviate

(3) Menshutkin, *J. Russ. Phys.-Chem. Soc.*, 41, 1089 (1909).

(4) Norris and Rubinstein, *THIS JOURNAL*, 61, 1163 (1939).

(5) P. C. Terwogt, *Z. anorg. Chem.*, 47, 203 (1905).

(6) Kaveler and Monroe, *THIS JOURNAL*, 50, 2421 (1928).

(7) Sugden, *J. Chem. Soc.*, 125, 27 (1924).