Oxynicotine.—Oxynicotine was prepared from hydrogen peroxide and nicotine according to the method of Pinner and Wolffenstein.[8] The crude oxynicotine was washed with acetone until a pure white product was obtained. The picrate was prepared and recrystallized from hot water, m. p. 169°. A mixture with the crystalline picrate obtained from the irradiation products of nicotine also melted at 169°.

A solution of 0.196 g. of oxynicotine was treated with 1 g. of stannous chloride and 5 cc. of concd. hydrochloric acid for one hour at room temperature. Excess barium hydroxide was then added and the solution was distilled with steam. Nicotine was determined in the distillate with silicotungstic acid; recovered 0.154 g. of nicotine (85.1%). The picrate melted at 222°, and a mixture with nicotine dipicrate melted at 222°. The rotation was determined in dilute water solution, $[\alpha]^{25}D$ −75°.

Summary

1. Oxynicotine, methylamine and nicotinic acid are formed during the ultraviolet irradiation of nicotine.

2. The oxynicotine formed by irradiation is identical with that formed by the hydrogen peroxide oxidation of nicotine.

3. Oxynicotine can be reduced to optically active nicotine.

RICHMOND, VIRGINIA RECEIVED SEPTEMBER 19, 1940

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Densities and Refractive Indices of Liquid Paraffin Hydrocarbons[1]

BY MAURICE L. HUGGINS

Many studies have been made of relationships between the structures of hydrocarbons and their densities and refractive indices. Nevertheless, in view of the recent publication[2-10] of extensive tables giving these properties for many compounds for which data have not been available until recently, a new attack on the problem would seem to be in order. This paper reports some results of such an attack. It deals only with *densities* (in g./cc. and *refractive indices* (for the sodium D lines) of *paraffin* hydrocarbons in the *liquid* state at 20°C.

Density

Kurtz and Lipkin[11] have recently made a careful and valuable study of the densities and molecular volumes of saturated hydrocarbons, using most of the new data. They deduced the equations

$$V = 32.2 + 16.26n \quad (1)$$

for normal paraffins, and

$$V = 31.2 + 16.28n \quad (2)$$

for all paraffins, the constants being averages computed from experimental data for many compounds. Here, n is the number of carbon atoms in the molecule, and V is the molal volume, related by definition to the density ρ and the molecular weight M by the equation

$$V = \frac{M}{\rho} \quad (3)$$

This paper, insofar as it deals with densities, may be considered an extension and refinement of Kurtz and Lipkin's work, in an attempt to correlate the structural details of the paraffin molecules with their volumes.

Although the experimental data for normal paraffins agree fairly well with a linear equation of the form of Equation 1, as shown in Fig. 1, the values for the short chain compounds show significant deviations. This is evident from an inspection of Fig. 2. To agree with any equation of the form of Equation 1, the points should fall on or near a straight line. Good agreement—within the probable experimental error of most of the individual values—can be obtained by including a term of the form constant/n or, alternatively, constant/V. We tentatively choose the former, merely because it is simpler for our purpose.

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(11) S. S. Kurtz, Jr., and M. R. Lipkin, paper presented at the Boston meeting of the American Chemical Society, September, 1939.

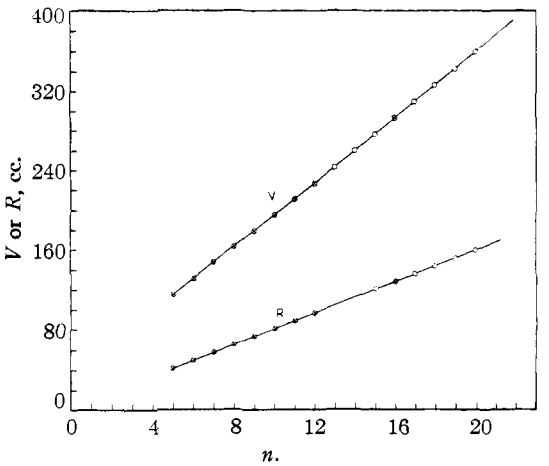

Fig. 1.—Molal volumes and refractions of normal paraffins. The curves represent Equations 4 and 8: ×, Egloff; O, Ward and Kurtz.

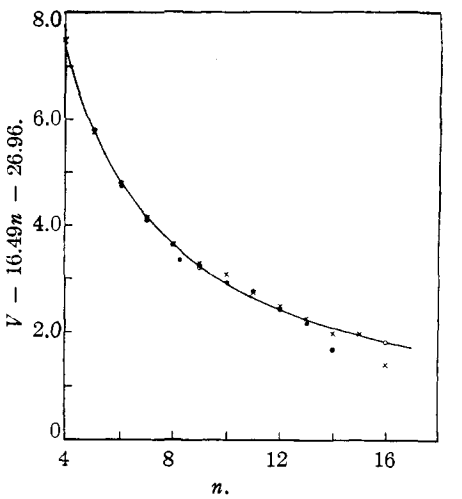

Fig. 2.—Illustrating the non-linearity of the relation between the molal volume and the chain length of normal paraffins. The curve represents Equation 4: ×, Egloff; ●, Ward and Kurtz; O, Wibaut, Hoog, Langedijk, Overhoff and Smittenberg.

The curves in Figs. 1 and 2 are drawn to satisfy the relation:

$$V_n = 26.96 + 16.49n + (29.0/n) \qquad (4)$$

This equation defines V_n, the *calculated* molal volume of the *normal* paraffin containing n carbon atoms.

The individual points of Fig. 2 represent experimental data as given by Ward and Kurtz,[9] by Egloff,[6] and by Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg.[10] Ward and Kurtz's data which were quoted from Grosse and Egloff[7] are omitted here and elsewhere in this paper, since they should presumably be superseded by the later Egloff[6] values.

A term corresponding to the $29.0/n$ term of Equation 4 should obviously be included in the expressions for the molal volumes of paraffins other than the normal ones, and of their derivatives also. Whether constant/n or constant/V or some more complex term is best is difficult to determine with the data now at hand. For the present, we assume the same term, $29.0/n$, for all.

Equation 4 is obviously equivalent to

$$V_n = 29.97N_{CH_3} + 16.49N_{CH_2} + (29.0/n) \qquad (5)$$

in which N_{CH_3} and N_{CH_2} are the numbers of CH_3 and CH_2 groups, respectively, in the molecule. One might perhaps expect a similar equation, with one additional term for CH groups and another for C atoms attached only to other carbons, to hold for paraffins in general. This is not accurately the case. The effect on the molal volume of the position of the CH or C relative to the rest of the molecule is by no means negligible. This effect is a complicated one and a thoroughly satisfactory solution to the problem has not been reached. For several series of compounds, however, the difference between the actual molal volume and the molal volume calculated by means of Equation 4, for the corresponding *normal* paraffin, is apparently a constant, practically within the probable experimental error (Fig. 3).

Besides the Egloff[6] and Ward and Kurtz[9] densities, used in preparing Fig. 3, others have been considered, especially those published by Wibaut, Hoog, Langedijk, Overhoff and Smittenberg[10] and by Brooks and co-workers[3,4] at the National Bureau of Standards. Densities at 20° also have been estimated in a number of instances from experimental measurements at a slightly higher temperature. Considering all these data, the average values of $V - V_n$ listed in Column 2 of Table I have been deduced.

TABLE I

Skeleton formula	$V - V_n$	$\overline{\lvert\rho(\text{obsd.}) - \rho(\text{calcd.})\rvert}$ Ref. 9	Ref. 6
C_n $(n>4)$	0	0.00026 (10)	0.00031 (12)
C_mCC $(m>1)$	+1.15	.0006 (6)	.0009 (5)
C_mCCC $(m>2)$	− .7	.0003 (4)	.0013 (4)
$C_mC(C)C$ $(m>1)$	+2.0	.0008 (3)	.0006 (3)

Columns 3 and 4 of Table I give averages of the difference between the experimental densities and those computed from the $V - V_n$ constants of Column 2. The number in parentheses is, in each

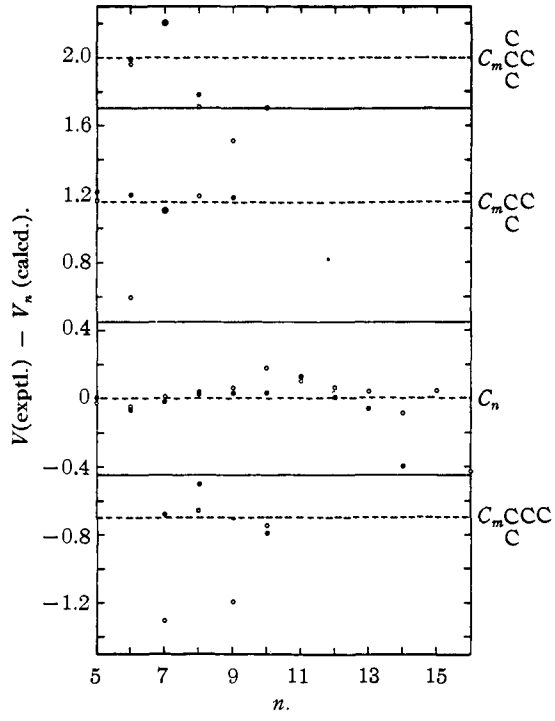

Fig. 3.—Deviations of experimental molal volumes from the values calculated by Equation 4 for the normal compounds having the same number of carbon atoms: O, Egloff; ●, Ward and Kurtz.

case, the number of compounds averaged. In general, the calculated density may be expected to agree with an accurate experimental value to within a few units in the fourth decimal place, for hydrocarbons of the classes listed.

Rough values of $V - V_n$ for various series other than those included in Table I can be estimated from the figures which have been collected for individual compounds. A further extension of Table I, however, hardly seems warranted until more densities and more reliable densities are available for substances of other types.

Refractive Index

The molal refraction of a compound may be defined in various ways. We have made extensive calculations, using the two definitions represented by the equations

$$R = V(n_D - 1) \quad (6)$$

and

$$R' = V(n_D^2 - 1) \quad (7)$$

concluding that, for our present purpose, there is little to choose between them. In this paper we use only the simpler definition, that of Equation 6.

Within the probable experimental error (see Figs. 1 and 4), the molal refraction of normal paraffins conforms to the equation

$$R_n = 2.12 + 7.815n = 8.875N_{CH_3} + 7.815N_{CH_2} \quad (8)$$

Computing $R - R_n$ for the non-normal paraffins and grouping the results together, as in dealing with molal volumes, one again finds approximate constancy within each series (Fig. 4). This is, of course, to be expected.

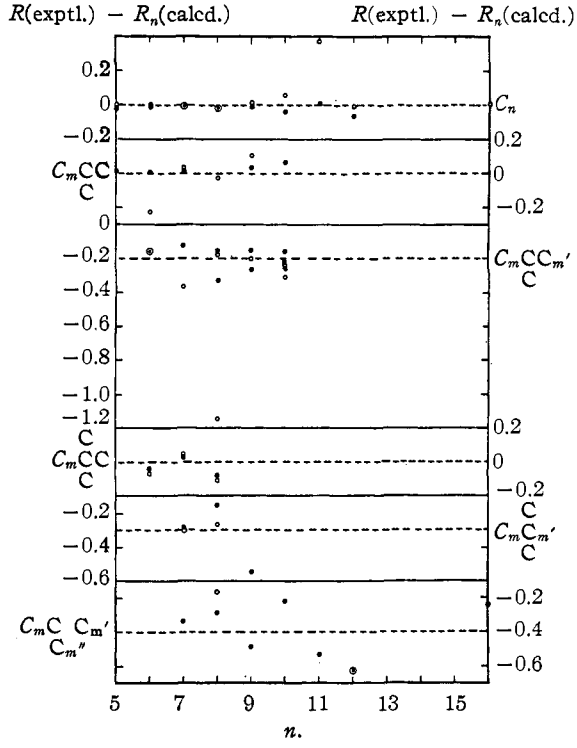

Fig. 4.—Deviations of experimental molal refractions from the values calculated by Equation 8 for the normal compounds having the same number of carbon atoms: O, Egloff; ●, Ward and Kurtz.

The refraction of such compounds as these is known to be due largely to the valence electrons, which, in the paraffins, are all bonding electrons. The experimental data are not in agreement with the assumption that all C–C bonds are equivalent and all C–H bonds are likewise equal to each other, as regards their contributions to the refraction.

The next simplest reasonable assumption is that the contribution of a bond to the refraction depends also on the number of radicals (or carbon atoms) attached to each of the carbon atoms concerned. According to this assumption, there would be 13 different bond types, each contributing a characteristic amount (α_{1H} for a bond between a hydrogen and a methyl carbon, α_{2H} for one between a hydrogen and a methylene carbon, α_{11} for one between two methyl carbons, etc.)

TABLE II

Skeleton formula	$R - R_n$	$\overline{\lvert n_D(\text{exptl.}) - n_D(\text{calcd.})\rvert}$ using exptl. densities Ref. 9	Ref. 6	using calcd. densities Ref. 9	Ref. 6
C_n	0	0.00012 (8)	0.00026 (9)	0.00016 (8)	0.00033 (9)
C_mCC C	$k_1 = 0$	.00013 (5)	.00067 (4)	.00028 (5)	.00024 (4)
$C_mCC_{m'}$ C	$k_2 = -0.2$	.00033 (9)	.00120 (7)	.00028 (4)	.00019 (3)
C C_mCC C	$k_3 = 0$	.00032 (3)	.00047 (3)	.00019 (3)	.00022 (3)
C $C_mCC_{m'}$ C	$k_4 = -0.3$	.00079 (3)	.00010 (2)		
Others		.00060 (28)	.00062 (22)		
All		.00047 (63)	.00064 (49)	.00022 (20)	.00027 (19)

to the total refraction:

$$R = \sum \alpha \tag{9}$$

The number of constants to be determined can be reduced by three by assuming further that

$$\alpha_{31} = \alpha_{22} \tag{10}$$

$$\alpha_{41} = \alpha_{32} \tag{11}$$

and

$$\alpha_{42} = \alpha_{33} \tag{12}$$

Neglecting α_{11} (since this applies only to ethane, for which no data are available), there remain nine constants. One may be fixed arbitrarily, insofar as the calculation of molal refractions of paraffins is concerned. Six may be determined from the two constants ($a = 2.12$ and $b = 7.815$) of Equation 8 and four average values of $R - R_n$ (*e. g.*, those designated as k_1, k_2, k_3 and k_4 in Table II). The other two (α_{43} and α_{44}) may be estimated by extrapolation of the curve of α *vs.* the sum of its subscripts.

For the arbitrary constant we take δ, defined by the equation

$$\delta = \alpha_{21} - \alpha_{22} \tag{13}$$

Writing the expressions for R in terms of the α's for the type structures concerned and making appropriate additions and subtractions, the following equations are readily deduced

$$\alpha_{21} = \frac{b-a}{2} + 3k_1 - 2k_2 - \frac{k_4}{2} + 5\delta = 3.397 + 5\delta \tag{14}$$

$$\alpha_{31} = \alpha_{22} = \frac{b-a}{2} + 3k_1 - 2k_2 - \frac{k_4}{2} + 4\delta = 3.397 + 4\delta \tag{15}$$

$$\alpha_{41} = \alpha_{32} = \frac{b-a}{2} + 2k_1 - k_2 - \frac{k_4}{2} + 3\delta = 3.197 + 3\delta \tag{16}$$

$$\alpha_{42} = \alpha_{33} = \frac{b-a}{2} + 2k_1 - k_2 - k_3 + \frac{k_4}{2} + 2\delta = 2.897 + 2\delta \tag{17}$$

$$\alpha_{1H} = \frac{b+a}{4} - \frac{k_1}{2} + \frac{k_2}{3} + \frac{k_4}{12} - \delta = 2.392 - \delta \tag{18}$$

$$\alpha_{2H} = \frac{b+a}{4} - \frac{3k_1}{2} + k_2 + \frac{k_4}{4} - 2\delta = 2.209 - 2\delta \tag{19}$$

$$\alpha_{3H} = \frac{b+a}{4} - \frac{5k_1}{2} + 2k_2 + \frac{3k_4}{4} - 3\delta = 1.859 - 3\delta \tag{20}$$

By extrapolation (Fig. 5)

$$\alpha_{43} = 2.50 + \delta \tag{21}$$

and

$$\alpha_{44} = 2.05 \tag{22}$$

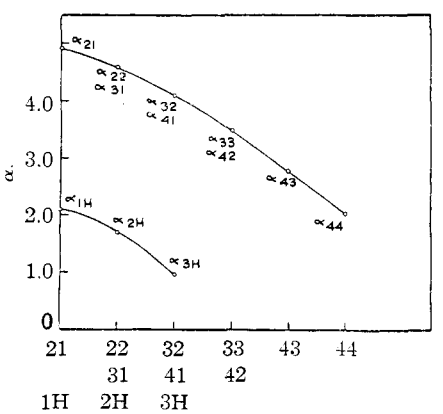

Fig. 5.—Dependence of the bond refraction on the kinds of atoms (hydrogen; primary, secondary, tertiary or quaternary carbon) joined by the bond, assuming $\delta = 0.30$.

From the above α values, the following equivalent relations readily can be deduced. (It is not necessary to assign a value to δ since this constant subtracts out.)

$$R = 7.815n + 1.06N_{CH_3} - 1.46N_{CH} - 3.02N_C - 0.10N_{CH\cdot CH} - 0.35N_{C\cdot C} - 0.20N_{CH\cdot C} + 0.20N_{CH\cdot CH_3} + 0.30N_{C\cdot CH_3} \tag{23}$$

$$R - R_n = -0.40N_{CH} - 0.90N_C - 0.10N_{CH\cdot CH} - 0.35N_{C\cdot C} - 0.20N_{CH\cdot C} + 0.20N_{CH\cdot CH_3} + 0.30N_{C\cdot CH_3} \tag{24}$$

The accuracy of these equations can be judged from the deviations of the experimental points from the dotted lines in Fig. 4, also from the average deviations between experimental and calculated refractive indices in Table II. With a few exceptions, which may be

largely the result of experimental inaccuracies, the agreement is quite good. In general, the refractive indices can be calculated, with or without measurements of the densities, to within a few units in the fourth decimal place. (It should be noted that none of the compounds for which reliable data are available contain bonds between two quaternary carbon atoms. Hence, there is as yet no check on the constant (-0.35) in the corresponding term of Equation 23 or Equation 24.)

Discussion

In many instances, the difference between experimental and calculated values, both for densities and for refractive indices, is less than the probable experimental inaccuracy. It seems hardly worth while to refine the treatment further than has been done, until more or better data are available. The calculations are, however, being extended to non-paraffin hydrocarbons and to other organic compounds.

A theoretical interpretation of the meaning of the regularities observed and of the magnitudes of the constants will be postponed until later. In the meantime, it is hoped that the equations obtained will prove useful.

Acknowledgment.—The writer is glad to acknowledge the able assistance of Miss Dorothy Owen with the calculations reported in this paper. He also wishes to express his indebtedness to Mr. S. S. Kurtz, Jr., of the Sun Oil Company, for a helpful discussion of some of the points involved in the present treatment.

Summary

1. Molal volumes of normal paraffins are given quite accurately by an equation of the form $V_n = a + bn + (c/n)$.

2. Molal volumes of several series of non-normal paraffins are given quite accurately by relations of the form $V = V_n + d$.

3. Molal refractions of paraffins in general are, quite accurately, the sums of characteristic bond refractions. The magnitude of a C–C or C–H bond refraction depends on the number of C and H atoms attached to each of the carbon atoms concerned. Simple equations for computing molal refractions (and refractive indices) of paraffins from their formulas have been deduced and tested.

KODAK RESEARCH LABORATORIES
ROCHESTER, NEW YORK RECEIVED AUGUST 7, 1940

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A New Optically Active Reagent for Carbonyl Compounds; the Resolution of *dl*-Camphor

BY ROBERT B. WOODWARD,[1] T. P. KOHMAN,[2] AND G. CHRIS HARRIS

Only a few instances of the resolution of racemic carbonyl compounds have been described in the literature. Using *l*-menthylhydrazine,[3] Neuberg[4] resolved *r*-arabinose, and shortly thereafter the same worker with Federer[5] accomplished the resolution of *r*-galactose, using *as*-phenyl-*d*-amylhydrazine.[6] Wilson, *et. al.*, have succeeded in resolving *r*-benzoin through its derivatives with δ-[*d*-(α-phenylethyl)]-semicarbazide and its enantiomer,[7a] δ-(*l*-menthyl)-semicarbazide,[7b] and δ-[*d*-(α-phenylpropyl)]-semicarbazide,[7c] but were not able to resolve *dl*-camphor, or *dl*-3-methylcyclohexanone with these reagents.

Several optically active hydrazine derivatives whose value as resolving agents has not been demonstrated, but which might potentially be of use in this connection, have been described, *viz.*, *d*-bornyl-hydrazine,[8] *as*-methyl-*d*-bornylhydrazine,[9] *as*-ethyl-*l*-menthylhydrazine,[3] ψ-camphorylsemicarbazide,[10] *l*-menthylglycine hydrazide,[11] and *d-neo*-menthylglycine hydrazide.[11] Of these compounds (including those used successfully by Neuberg and Wilson) several have not been obtained in a state of purity, the majority are oils or low-melting solids, and, with the exception of the last three, the substances are unstable either in

(1) Member of the Society of Fellows.

(2) Mr. Kohman participated in this research in pursuance of a Chemistry 5 special problem.

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