[Contribution from the Laboratory of the Ethyl Gasoline Corporation]

THE PREPARATION AND PROPERTIES OF THE ISOMERIC HEPTANES. PART II. PHYSICAL PROPERTIES

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I. Introduction

In Part I of this paper[1] the preparation and purification of the nine isomeric heptanes were reported, together with certain data on the physical properties commonly employed for purposes of identification. In Part II there are presented measurements obtained in this Laboratory on other properties, together with a summary of the data of other investigators to whom samples of these hydrocarbons were loaned. Some of these data have been published and others are presented prior to publication elsewhere by the courtesy of the investigators in question, to whom acknowledgment is made below. The entire available data are summarized for the purpose of discussing the effect of structure upon the physical properties, since few trustworthy data are available on this point for the paraffin hydrocarbons and since the group in question is large enough to cover a wide variety of structural types. Further data are being accumulated on other properties of these hydrocarbons, but as the results of these investigations seem likely to be unavailable for some time to come, it has not been thought advisable to delay further the present publication.

II. Experimental Methods

(a) Densities, boiling and melting points are discussed in Part I of this paper.

The data on refractive indices, dispersions, dielectric constants and viscosities are taken from Smyth and Stoops,[2] where data additional to those quoted herein may be found.

(b) Surface tensions were measured in this Laboratory, employing essentially the technique of Richards, Speyers and Carver.[3]

In order to check the accuracy of the data, measurements were made of the surface tension of normal octane, which agreed well with those of Richards, Speyers and Carver, and of pure benzene, which agreed well with the data in "International Critical Tables." The measurements were made at one or more temperatures within a degree or two of 20°, and were extrapolated to this temperature.[4]

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[1] Edgar, Calingaert and Marker, This Journal, **51**, 1483 (1929).

[2] Smyth and Stoops, *ibid.*, **50**, 1883 (1928).

[3] Richards, Speyers and Carver, *ibid.*, **46**, 1196 (1924).

[4] These measurements were made by Mr. F. J. Dykstra, to whom the authors are indebted. The authors also desire to acknowledge the loan of a cathetometer for this work by the Department of Physics of New York University.

(c) Critical temperatures and pressures were measured by Professor F. G. Keyes and Dr. R. V. Kleinschmidt, to whom the authors are much indebted both for the measurements and for permission to include the data in this paper, prior to publication elsewhere. The apparatus and technique were essentially those described by Keyes, Taylor and Smith.[5] At the time these measurements were made, 3,3-dimethylpentane had not been prepared and no critical data concerning it are available. The coefficient a and b of van der Waals' equation (Cols. 12 and 13) were calculated from these data, as were the values of the Guldberg function T_c/T_B (Col. 11).

(d) The coefficients of thermal expansion were measured in this Laboratory by Mr. O. R. Dorion, to whom the authors are indebted. The apparatus consisted of a dilatometer of Pyrex glass, with a bulb of about 6 cc. capacity and a capillary of such dimensions as to give about 30 cm. rise in the liquid level of the hydrocarbons for 20° temperature rise. The dilatometer was calibrated by filling it with a known weight of distilled water and reading the liquid level in the capillary at different temperatures, readings being made with a cathetometer. Density data for water were taken from "International Critical Tables," and appropriate corrections were made for the thermometer employed and for the expansion of the glass. The dilatometer was then filled with weighed amounts of the hydrocarbons and the liquid level in the capillary was measured at various temperatures from 10 to 30°. Since for the purpose of this paper the relative coefficients of expansion of the hydrocarbons were more important than their absolute values, the following method was employed in treating the data. The liquid level readings in the capillary were plotted on large scale coördinate paper against the temperature and from the curves thus obtained temperature differences were read corresponding to the same definite segment of the capillary between two fixed marks. The bulb was in all cases filled to such an extent that the segment corresponded approximately to the temperature range of 15 to 20°. The hydrocarbons are so nearly alike in their expansion coefficients that the actual temperatures involved were seldom as much as a degree different for the different hydrocarbons. A value for the coefficient of expansion of normal heptane was then selected as a mean from density determinations at temperatures above and below 20° by the authors (Part I), from the data of Smyth and Stoops[2] and from the dilatometer dimensions. The values for the isomers were then computed by comparing the temperature differences above mentioned with that for normal heptane. The data are given to four significant figures and are almost certainly correct to three. The supply of 3,3-dimethylpentane was exhausted when these measurements were made, and its density–temperature coefficient was taken as the average for the other eight isomers, that is, 0.000848. This value is probably very nearly correct,

[5] Keyes, Taylor and Smith, *J. Math. Phys., Mass. Inst. Tech.*, **1**, 311 (1921).

since it is equal to that of the 2,3-isomer, which, as will be shown in the discussion below, shows properties very similar to those of the 3,3-isomer.

The temperature coefficients of density in the neighborhood of 20° had already been determined for most of the hydrocarbons, but it was felt that values calculated from the coefficients of thermal expansion were more nearly accurate than the direct measurements, and the figures in Col. 4 are calculated in this way.

(e) The velocity of sound through the hydrocarbons and the coefficient, β_φ, of adiabatic compressibility, were measured by E. B. Freyer, J. C. Hubbard and D. H. Andrews.[6]

The coefficients of isothermal compressibility, β_T, were calculated by the equation $\beta_T = \beta_\varphi + \frac{(\mathrm{d}v/\mathrm{d}t)^2\,\mathrm{d}T}{J\,C_p}$, where J is the mechanical equivalent of heat, C_p the specific heat, v the specific volume and d the density. In the absence of specific heat data for most of the isomers the value of 0.50 cal. per g. for normal heptane was employed in all calculations. Later data on actual specific heats may alter the computed values slightly.

(f) Heats of combustion were determined by the U. S. Bureau of Standards.[7] They were made in a bomb calorimeter and are defined as the heat liberated in 20° calories per gram of liquid hydrocarbon weighed in air, the products of combustion being cooled to the initial temperature and the water condensed to the liquid state. The data are believed to be accurate to 0.2% or better.

(g) Molecular diameters and lengths were calculated by Stewart from X-ray diffraction data.[8]

(h) Critical solution temperatures in aniline were determined in this Laboratory. Aniline was dried over solid potassium hydroxide and was freshly distilled before each determination. The hydrocarbons were also dried over solid potassium hydroxide.

The mixtures of aniline and hydrocarbon were heated in a small test-tube fitted with an Anschütz thermometer, the whole being jacketed by another test-tube, which in turn was immersed in a water-bath. The aniline and hydrocarbon were weighed into the test-tube and the weight was checked after the determination in order to ascertain whether appreciable loss due to volatilization of hydrocarbon had occurred. The proportions of aniline and hydrocarbon were altered through a range sufficient to pass through the maximum point on the solubility–temperature curve.[9] The data are expressed graphically in Fig. 1.

[6] Freyer, Hubbard and Andrews, THIS JOURNAL, **51**, 759 (1929).

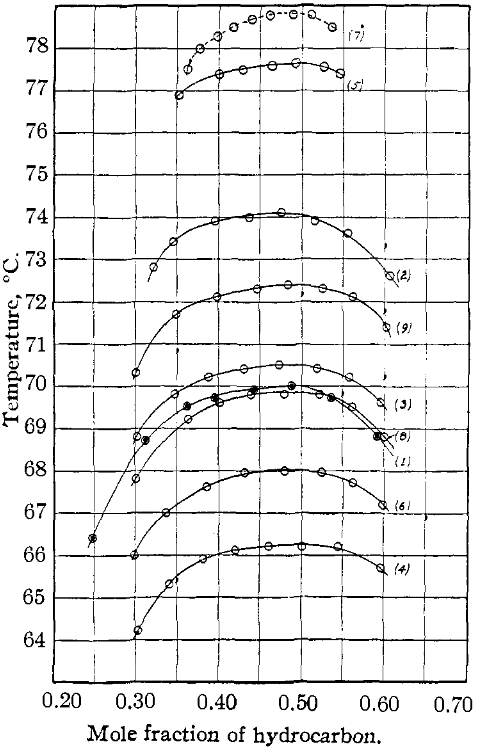
[7] Bureau of Standards Journal of Research, **2**, 373 (1929).

[8] S. W. Stewart, *Phys. Rev.*, **32**, 153 (1928).

[9] These determinations were made by Mr. D. T. Flood, to whom the authors are indebted.

III. Experimental Data

Table I contains the experimental data referred to above, together with certain functions derived from the data. Table II summarizes the order in which these properties and functions vary with the structure of the hydrocarbons. Table III contains such data as are available from the literature on the properties of the hexanes, octanes, nonanes and decanes. Only such data are given as are available for a number of the isomers, since the data are used for comparison of the effect of structure on the properties of the hydrocarbons as compared with the heptanes. The data have been taken from what seemed to be the most reliable sources, some from "International Critical Tables," some from Beilstein and some from the original literature. The data have been extrapolated when necessary.



(1), *n*-Heptane; (2), 2-methylhexane; (3), 3-methylhexane; (4), 3-ethylpentane; (5), 2,2-dimethylpentane; (6), 2,3-dimethylpentane; (7), 2,4-dimethylpentane; (8), 3,3-dimethylpentane; (9), 2,2,3-trimethylbutane.

Fig. 1.—Critical solution temperatures of the heptanes in aniline.

* Because of the extremely small amount of 2,4-dimethylpentane which was available when these measurements were made it was not possible to determine accurately the values of the mole-fractions corresponding to the temperatures given. The curve must therefore be regarded as approximate as far as the mole-fraction data are concerned.

IV. Discussion

(a) **General.**—Very few of the data given in Table I are available in the literature. With the exceptions noted in Part I of this paper, the data in general agree very well with the most reliable data which are available. Since the chief purpose of this paper is to discuss the effect of structure upon physical properties, further comparison of the individual data with those in the literature has been omitted.

Very few generalizations have been possible heretofore concerning any relations which may exist between the structure of paraffin hydrocarbons

TABLE IA

PHYSICAL PROPERTIES OF THE HEPTANES

No.	Name	(1) B. p., °C. (760 mm.)	(2) M. p., °C.	(3) d^{20}_4	(4) $\Delta d/\Delta t$ (20°C.)
1	*n*-Heptane	98.4	− 90.5	0.6836	0.000835
2	2-Methylhexane	90.0	−119.1	.6789	.000855
3	3-Methylhexane	91.8	.....	.6870	.000844
4	3-Ethylpentane	93.3	.....	.6984	.000853
5	2,2-Dimethylpentane	78.9	−125.6	.6737	.000855
6	2,3-Dimethylpentane	89.7	.....	.6952	.000848
7	2,4-Dimethylpentane	80.8	−123.4	.6745	.000856
8	3,3-Dimethylpentane	86.0	−135.0	.6934	.000848[a]
9	2,2,3-Trimethylbutane	80.9	− 25.0	.6900	.000838

[a] Assumed value, see paragraph d, section II.

TABLE IB

PHYSICAL PROPERTIES OF THE HEPTANES

No.	(5) $n^{20°}_D$	(6) MR_D	(7) $MR_\gamma - MR_\alpha$	(8) Dielec. const. ϵ, at 20°	(9) t_c, °C.	(10) P_c, atm.	(11) T_c/T_B	(12) $a \times 10^{-7}$ (van d. Waals)
1	1.38777	34.54	0.84	1.930	269.5	27.65	1.460	3.025
2	1.38509	34.57	.85	1.922	257.9	27.2	1.462	2.945
3	1.38873	34.45	.83	1.930	262.4	28.1	1.467	2.900
4	1.39366	34.27	.82	1.942	267.6	28.6	1.479	2.905
5	1.38233	34.61	.86	1.915	247.7	28.4	1.480	2.727
6	1.39201	34.31	.83	1.942	264.6	29.2	1.493	2.814
7	1.38233	34.57	.85	1.917	247.1	27.4	1.470	2.813
8	1.39114	34.32	.83	1.940	...	...	...	...
9	1.38940	34.35	.84	1.930	258.3	29.75	1.497	2.697

n = index of refraction. $MR = (n^2-1)/(n^2+2) \times 1/d$. $MR_\gamma - MR_\alpha$ = molecular dispersion for the hydrogen α and γ lines.

TABLE IC

PHYSICAL PROPERTIES OF THE HEPTANES

No.	(13) b (cc.) van d. Waals	(14) a/V^2	(15) Vel. of sound at 20° m/sec.	(16) β_φ (20°) atm. × 10^6	(17) β_T (20°) × 10^6	(18) $\alpha \times 10^5$	(19) $\alpha/\beta_T \times 293$	(20) $(5200+30t_B)/V$
1	201.4	1415	1154.0	111.4	142.37	122.2	2513	55.73
2	200.3	1358	1120.0	119.05	152.20	125.9	2424	53.62
3	195.5	1368	1135.5	114.45	145.62	122.8	2471	54.64
4	193.9	1417	1169.5	106.15	136.46	122.2	2621	55.87
5	188.1	1232	1080.0	128.90	162.79	126.8	2282	50.98
6	188.9	1360	1148.5	110.70	140.68	122.0	2541	54.86
7	194.8	1280	1083.5	128.00	161.85	126.8	2296	51.42
8	...	...	1129.5	114.55	145.13	122.3[a]	2467	53.95
9	183.2	1284	1101.5	121.05	151.44	121.5	2351	52.63

[a] Assumed value.

V = the molecular volume. B_φ = the adiabatic compressibility in cc./cc./atm. β_T = the isothermal compressibility in cc./cc./atm. α = the coefficient of thermal expansion in cc./cc./°C.

TABLE ID

PHYSICAL PROPERTIES OF THE HEPTANES

No.	(21) Surf. tens., 20°, γ,dynes/cm.	(22) $\gamma/V^{1/3}$	(23) C.T.S., aniline, °C.	(24) η 20°	(25) Mol. diam., cm. × 10^8	(26) Mol. length, cm. × 10^8	(27) Ht. of comb., cal./g.
1	20.28	3.848	70.0	0.00409	4.64	11.38	11490
2	19.37	3.668	74.1	.00378	4.84, 5.25	10.47, 8.87	11480
3	19.56	3.718	70.5	.00372	5.68	7.46	11480
4	20.16	3.854	66.3	.00377	5.51	7.84	11490
5	17.80	3.362	77.7	.00385	5.68	7.61	11470
6	19.65	3.750	68.1	.00406	5.68	7.38	11480
7	17.93[a]	3.388[a]	78.8	.00361	5.68	7.61	11480
8	19.63	3.743	71.0	.00454	5.68	7.38	11470
9	18.60	3.541	72.4	.00585	5.69	7.45	11470

γ = the surface tension in dynes per cm. η = the absolute viscosity. C.T.S. aniline = the critical solution temperature in aniline at the concentration giving the maximum temperature.

[a] There is some uncertainty as to the state of purity of the sample used for this particular measurement. The data, however, fall in an order which agrees with the other properties.

TABLE II

ORDER IN WHICH THE PHYSICAL PROPERTIES OF THE HEPTANES VARY

l = lowest value; h = highest value

(a)	d	5	7	2	1	3	9	8	6	4	l−h
	n_D	(5	7)	2	1	3	9	8	6	4	l−h
	MR	5	7	2	1	3	9	8	6	4	l−h
	$Mr_\gamma - MR_\alpha$	5	(7	2)	(1	9)	(3	8	6)	4	l−h
	ϵ	5	7	2	(1	3	9)	8	(6	4)	l−h
(b)	$\gamma/V^{1/3}$	5	7	9	2	3	8	6	1	4	l−h
	$(5200-30t_B/V)$	5	7	9	2	8	3	6	1	4	l−h
	a/V^2	5	7	9	2		6	3	1	4	l−h
	α/β_T	5	7	9	2	8	3	1	6	4	l−h
	C.T.S.	7	5	2	9	8	3	1	6	4	h−l
(c)	γ	5	7	9	2	3	8	6	4	1	l−h
	β_φ	5	7	9	2	3	8	1	6	4	h−l
	β_T	5	7	2	9	3	8	1	6	4	h−l
	Vel. sound	5	7	9	2	3	8	6	1	4	l−h
	T_c	5	7	2	9	3		6	4	1	l−h
	B. p.	5	7	9	8	6	2	3	4	1	l−h
(d)	P_c	2	7	1	3	5	4	6	9		l−h
	a	9	5	7	6	3	4	2	1		l−h
	b	9	5	6	4	7	3	2	1		l−h
	T_c/T_B	9	6	5	4	7	3	2	1		h−l
	η	7	3	4	2	5	6	1	8	9	l−h

(a), Density, refraction, dielectric properties and functions; (b), functions and properties directly measuring internal pressure; (c), properties and functions relating to internal pressure and following essentially the same order; (d), miscellaneous properties and functions.

TABLE III

PHYSICAL PROPERTIES OF HEXANES

* = Extrapolated

No.	Name	B. p., °C.	d_4^{20}	n_D^{15}	η_{20}	C.T.S. Aniline	Compr. (20°) 100–300 atm.
1	*n*-Hexane	68.95[a]	0.6595*[b]	1.3760*[c]	0.00320[d]	68.9[a]	117.5[e]
2	2-Methylpentane	60.2[a]	.6542*[a]	1.37445[b]	.00310[d]	74.7[a]	119.0[e]
3	3-Methylpentane	63.2[a]	.6647*[a]	1.37929[b]	.00322[d]	69.4[a]	...
4	2,2-Dimethylbutane	49.7[a]	.6498*[a]	1.37158[b]	.00375[d]	80.75[a]	...
5	2,3-Dimethylbutane	58.1[a]	.6618*[a]	1.38092[b]	.00385[d]	72.3[a]	...

PHYSICAL PROPERTIES OF OCTANES

No.	Name	B. p., °C.	d_4^{20}	n_D^{20}	C.T.S. aniline	Compr. (20°) 100–300 atm.	η_{20}
1	*n*-Octane	124.6[c]	0.702*[c]	1.3980[c]	72.0[h]	95.7[e]	21.88[g]
2	2-Methylheptane	116.0[c]	.6985[i]	1.3935[i]	74.0[h]	101.0[e]	20.98[g]
3	3-Methylheptane	122.2[c]	.707[c]	.....	...	....	...
4	4-Methylheptane	118.0[c]	.722[c]	1.398[c]	...	....	...
5	3-Ethylhexane	118.8[c]	.713*[i]	1.4016[c]	...	96.0	...
6	2,3-Dimethylhexane	114.0[c]	.720*[c]	1.4093[c]	...	....	...
7	2,4-Dimethylhexane	109.9[c]	.703*[c]	1.4026[c]	...	....	...
8	2,5-Dimethylhexane	109.2[c]	.696*[i]	1.3929[c]	...	105.0[e]	20.02[g]
9	3,4-Dimethylhexane	116.5[c]	.721[c]	1.4058[c]	...	94.5[e]	...
10	2-Methyl-3-ethylpentane	114.0[c]	.704*[c]	1.4016[c]	...	....	...
11	2,2,3-Trimethylpentane	110.8[c]	.717*[c]	1.4184[c]	...	....	...
12	2,2,4-Trimethylpentane	99.3[j]	.6918[k]	1.3916[k]	...	....	...

PHYSICAL PROPERTIES OF THE NONANES

No.	Name	B. p., °C.	d_4^{20}
1	*n*-Nonane	150.6[c]	0.718[c]
2	3-Methyloctane	143.4[c]	.719*[c]
3	4-Methyloctane	141.6[c]	.727*[c]
4	4-Ethylheptane	139.0[c]	.737*[c]
5	3,3-Diethylpentane	139.2[l]	.7522[l]
6	2,4-Dimethylheptane	133.3[c]	.716*[c]
7	2,5-Dimethylheptane	135.9[c]	.714*[c]
8	2,6-Dimethylheptane	132.0[c]	.707*[c]
9	2,2,5-Trimethylhexane	126.0[i]	.707*[i]

PHYSICAL PROPERTIES OF THE DECANES

No.	Name	B. p., °C.	d_4^{20}
1	*n*-Decane	174.0[c]	0.730*[i]
2	2-Methylnonane	160.0[c]	.724*[c]
3	3-Methylnonane	166.9[c]	.735[c]
4	5-Methylnonane	166.2[c]	.732[c]
5	4-Propylheptane	161.7[c]	.736*[c]
6	2,6-Dimethyloctane	160.5[i]	.729[i]
7	2,7-Dimethyloctane	160.0[c]	.722[c]
8	3,6-Dimethyloctane	160.8[c]	.730*[c]
9	2,2,6-Trimethylheptane	152.0[i]	.721[i]

[a] Chavanne, *Bull. soc. chim. Belg.*, **31**, 331 (1922); [b] Lowry, *J. Chem. Soc.*, **105,** 91 (1914); [c] "International Critical Tables;" [d] Chavanne and van Risseghem, *Bull.*

and their physical properties, since the experimental data have been very fragmentary and none too reliable. Most generalizations previously reported have referred to the effect of increasing molecular weight in the normal hydrocarbons, to such facts as that the boiling point of the normal hydrocarbon is higher than those of the known isomers and to a few scattered facts concerning the relations between the normal hydrocarbon and the simple "iso"-hydrocarbons. The data herein presented give an opportunity for a much more complete analysis of such relationships.

Thus inspection of Tables I and II shows certain striking regularities in the order in which the physical properties vary with the structure. For the purpose of simplifying the discussion each hydrocarbon has been given a number, and the structures corresponding to these numbers are contained in Table I.

(b) **Density, Refraction and Dielectric Constant.**—If we consider first density, index of refraction and dielectric constant, the isomers fall in an order which is essentially identical for all the properties. The order is still noticeable in properties which are known with less accuracy, coefficient of expansion and dispersion, and even in functions calculated from these constants and which are considered in general to be independent of structure, molecular refraction, molecular dispersion and polarization.

It would seem, therefore, that they must correspond to a definite influence of the structural arrangement of the atoms in the molecule. Thus the values of each function of this group for the normal hydrocarbon occupy an intermediate position. A methyl group located in the 2-position decreases the value of each function below that of the normal hydrocarbon, while a methyl group located in the 3-position increases the value of each function. Similarly, two methyl groups in the 2-position (either on the same carbon atom, or at corresponding positions at each end of the pentane chain) decrease still further the values of the function, while two methyl groups in the 3-position, or an ethyl group in the 3-position, increase still further the values of the functions above those of the normal hydrocarbon. When two groups are adjacent, however, the values of the various functions are always quite high relative to the normal. This effect appears in 2,3-dimethylpentane and in 2,2,3-trimethylbutane, and will be discussed further below.

The order in which the hydrocarbons fall when arranged in accordance with the variation of their properties of this group is essentially 5 7 2 1 3 9 8 6 4, which will be referred to as Order 1.

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soc. chim. Belg., **31,** 87 (1922); [e] Richards, Steel, Mathews and Speyers, This Journal, **34,** 971, 988 (1912); [f] van Risseghem, *Bull. soc. chim. Belg.*, **31,** 62 (1922); [g] Hildebrand, "Solubility," The Chemical Catalog Company, Inc., New York, **1924;** Stewart, *Phys. Rev.*, **32,** 153 (1928); [h] Chavanne and Simon, *Compt. rend.*, **168,** 1112, 1324 (1919); [i] Beilstein, 4th ed., Suppl., Vol. I; [j] Graham Edgar, *Ind. Eng. Chem.*, **19,** 145 (1927); [k] Smyth and Stoops, This Journal, **50,** 1883 (1928); [l] Morgan, Carter and Duck, *J. Chem. Soc.*, **127,** 1252 (1925); Lowry, *ibid.*, **127,** 1215 (1925).

(c) **Internal Pressure.**—It has been shown by Hildebrand[10] that relative internal pressures may be calculated approximately from surface tension, from the boiling point, from van der Waals' constant, *a*, from the ratio of the coefficients of thermal expansion to isothermal compressibility and from the critical solution temperatures in a non-polar solvent. If we consider these various functions (Cols. 19, 20, 22 and 23), we find the isomers falling in a nearly identical order 5 7 9 2 8 3 6 1 4, which will be referred to as Order 2.

Considering the uncertainty underlying the assumptions involved in the calculation of these functions, the agreement in Order 2 is striking.

As would be expected, the fundamental properties employed in the calculation of the internal pressures (Cols. 1, 9, 15, 16, 17 and 21) follow in general the same order, with somewhat greater variation, particularly with reference to the normal hydrocarbon, which varies between the extreme end position and the third position from the end.

(d) **Van der Waals' constants** *a* and *b* follow an order very close to that of the ratio of the critical temperature to the boiling point, which may indicate that their values vary with the temperature, and at corresponding temperatures might fall in line with the other properties.

(e) **The critical pressures and the viscosities** show no evidence of relation to any other property.

(f) **The heats of combustion** are clearly identical within the limit of error, 0.2% or 2000 cal. per mole. The heats of formation calculated therefrom are thus also identical, their value being 57,000 ±2000 cal. Obviously the experimental accuracy is not sufficient to determine whether or not small differences exist among the heats of formation of the isomers. It has been shown by Parks[11] that in the case of three isomeric octanes very substantial differences exist in the entropies, but the differences in the heats of formation must be small, if they exist at all.

(g) Regarding the arrangement of the atoms in space, some conclusions may be drawn from the X-ray diffraction data of Stewart. The addition of methyl or ethyl groups as side chains decreases the apparent length of the main chain and increases the apparent diameter by more than would be expected. It seems probable, therefore, that the substitution causes a twisting or bending back of the otherwise straight chain. The only exception to this rule is 9, in which the butane chain keeps its normal length. This is also the only case which has been investigated in which every carbon between the ends of the chain is substituted, which suggests that in that case the bending of the chain may be hindered by the closely packed side chains.

[10] Hildebrand, "Solubility," Chemical Catalog Co., Inc., New York, **1924**.

[11] G. S. Parks, paper delivered at American Chemical Society meeting at Swampscott, Massachusetts, September, 1928.

(h) It will be noted that the difference between Order 1 and Order 2 is entirely due to the change of position of the normal hydrocarbon (1) and the 2,2,3-trimethylbutane (9). If these two be omitted, the order of variation of the properties of both classes becomes surprisingly constant. These two compounds represent, of course, the two extremes of structural arrangement; nevertheless, the cause of their variation from the general arrangement is not clear.

It is interesting to speculate on the reasons for this orderly variation of physical properties with structure. From the thermodynamic standpoint no data are at present available, although it is hoped that the entropies of these compounds will be determined later. Judging from the data of Parks on three octanes,[11] the entropies of the branched-chain isomers should be lower than those of the normal hydrocarbons, but the relation to structure cannot be more than guessed at.

(i) **Hydrocarbons other than the Heptanes.**—The data discussed above for the heptanes is particularly useful for determining the effect of structure, because of the fact that each individual property was measured for all of the isomers by one experimenter, and hence the data are much more comparable than most of those given in the literature and taken from scattered sources. Nevertheless, consideration of the data in Table III on the properties of the hexanes, octanes, nonanes and decanes shows that the considerations indicated above for the heptanes hold very well for the other hydrocarbons.

Thus a methyl group in the 2-position decreases the specific gravity and refractive index below the normal hydrocarbon (with the exception of the hexanes, the data on refractive index are somewhat uncertain, and have been omitted entirely for the nonanes and decanes), while a methyl group in the 3-position increases these functions above that of the normal hydrocarbon. Two methyl groups in the 2-position (2,2-dimethylbutane, 2,5-dimethylhexane, 2,6-dimethylheptane and 2,7-dimethyloctane) decrease still further the specific gravity, while 2,3-dimethylbutane shows the effect of adjacent carbon atoms, as do 2,3- and 3,4-dimethylhexane.

Three methyl groups in the 2-position (2,2,4-trimethylpentane, 2,2,5-trimethylhexane and 2,2,6-trimethylheptane) have the lowest specific gravities reported, but when the groups are adjacent, as in the corresponding 2,2,3-trimethylbutane, the latter effect predominates.

In the octanes, nonanes and decanes a methyl group in the 4- or 5-position has an effect similar to one in the 3-position. An extreme case of the effect of substitution in the 3-position is shown by 3,3-diethylpentane.

Such other properties as are available agree well with the order of variation shown by the heptanes. Thus for the hexanes the critical solution temperatures in aniline follow the order shown for corresponding heptanes, as do the two which are available for the octanes. The available compressibilities and surface tensions follow the usual order, while the viscosities (available only for the hexanes) show the irregular variation exhibited by the heptanes.

The boiling points of the normal hydrocarbons are invariably the highest for the isomers, but the 2-substituted isomers always boil lower than the 3-substituted isomers, and those containing two or three methyl groups in the 2-position (at the same or opposite ends of the chain) boil lowest of all.

Altogether, although the data on the other paraffin hydrocarbons are not sufficiently complete to lay down any definite laws relating their structure to their properties, it is clear that so far as the data are available the regularities found in the heptanes are also found in the other hydrocarbons. It would appear probable, therefore, that approximate values of most of the physical properties of the paraffin hydrocarbons can be predicted with reasonable assurance when their structure is known.[12]

It is hoped that this investigation may be helpful in interpreting the characteristics of the paraffin hydrocarbons, and may eventually lead to clarifying these characteristics in terms of the energy relations and molecular dimensions involved.

Summary

1. Data on a number of the physical properties of the nine isomeric heptanes are presented, together with functions derived from the data.

2. Certain definite regularities are found relating the physical properties of the isomers to their structure.

3. The relationships between the structure of the heptanes and their physical properties exist also for the hexanes, octanes, nonanes and decanes, as far as the data are available.

4. These relationships enable the physical properties of paraffin hydrocarbons to be predicted with reasonable assurance from their structures.

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[12] An interesting example of such prediction is found in the case of normal decane. The specific gravity given in "International Critical Tables," Vol. I, seemed to the authors to be probably too high, as it is greater than that of any of the isomers. Examination of the literature confirmed this suspicion, and judging from the data on normal decane in Vol. III of "International Critical Tables," the value of the density in Vol. I is really for 0° instead of 20° as stated.