Table VI

Data and Values

Substance	Mn	O_2	MnO	Mn_3O_4	MnO_2
S_{298}	7.3	49.2	14.92	35.73	13.93

Reaction	ΔH	ΔS	ΔF
$Mn + {}^1/_2O_2 = MnO$	−90,900	−17.0	− 85,830
$3Mn + 2O_2 = Mn_3O_4$	−328,000	−84.6	−302,800
$Mn + O_2 = MnO_2$	−125,300	−42.6	−112,600

Summary

The specific heats of manganous and manganous–manganic oxides and of manganese dioxide have been measured from 70 to 300°K.

With the aid of the third law of thermodynamics, the free energies of these substances at 298° K. have been calculated.

[Contribution from the Department of Chemistry, Princeton University]

THE DIELECTRIC POLARIZATION OF LIQUIDS. III. THE POLARIZATION OF THE ISOMERS OF HEPTANE

By C. P. Smyth and W. N. Stoops

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Accurate measurements of the dielectric constants of methane, ethane and hexane over a wide range of temperature[1] have made it possible to calculate that the molecules of these substances have no electric moments and calculations made by an approximate method have also indicated the absence of an electric doublet in the molecules of octane and decane.[2] This is in accord with the fact that, according to calculations from molecular structure,[2] it should be possible to replace a hydrogen atom attached to a carbon atom by a methyl group without altering the electric symmetry of the molecule unless the bulk of the methyl group causes distortion of the structure or unless the methyl group itself is distorted due to small shifts of electrons in the field of a doublet already present. Since, with the exception of methane which, as the first member of the series, might be expected to be abnormal, all of the hydrocarbons studied had contained an even number of carbon atoms, it seemed desirable to investigate an odd member of the series, which, of course, would contain an even number of C–C bonds. Measurements made upon pure samples of all of the isomers of heptane very kindly loaned to us by Dr. Graham Edgar of the Ethyl Gasoline Corporation have made it possible to determine the electric symmetry of nine different arrangements of six C–C bonds. An octane, 2,2,4-trimethylpentane, loaned by Dr. Edgar, has also been studied.

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[1] (a) Sänger, *Physik. Z.*, **27**, 556 (1926); (b) Smyth and Zahn, This Journal, **47**, 2501 (1925); (c) Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

[2] Smyth, This Journal, **46**, 2151 (1924).

In the first of this series of papers[3] the method of obtaining the electric moment of the molecule of a substance has been discussed. The molar polarization of a substance, $P = (\epsilon - 1)/(\epsilon + 2) \times M/d = P_E + P_A + P_M$, in which ϵ = the dielectric constant, M = the molecular weight, d = the density, $P_E + P_A$ = the polarization due to shifts of charges in the molecule inducible by an external field and P_M = the polarization due to the orientation of the permanent electric doublets of the molecules. When P_M is 0, the moment of the molecule must be 0. P_E may be calculated as the molar refraction for light of infinite wave length, $MR_\infty = (1 - \lambda_0^2/\lambda^2)[(n^2 - 1)/(n^2 + 2) \times M/d]$, where n is the index of refraction for light of wave length λ and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. P_A, the difference between P_E, the polarization due to electronic shifts, and the total induced polarization, is commonly attributed to induced shifts of atoms or radicals.

The refractive indices were measured by Mr. E. W. Engel with the assistance of one of the writers. A Pulfrich refractometer was used and accurate temperature control was obtained by a flow of water from carefully regulated thermostats. A complete series of measurements was made for the sodium D line. A month later, after readjustment of the instrument and installation of a new prism, measurements were made again for the D line and also for the α, β and γ hydrogen lines. The new values for the D line showed an average difference from the old values of only 0.00009, the sign of the difference being disregarded. The molar refractions for the different wave lengths are given in Table I, with the refractive indices. These molar refractions were used to calculate the values of MR_∞, given in Table IV as P_E, by the substitution of the corresponding values of MR and λ. As four equations were thus obtained for each substance and only two were necessary in order to solve for MR_∞, a test of the equation and the data was made by calculating MR_∞ first from MR_γ and MR_α and then from MR_β and MR_D. Although this method of combining the values is the one best calculated to make any error apparent, the greatest difference found between the values obtained from the two pairs of refractions was 0.02. The dispersions calculated from these data are given in Table IV.

The densities and dielectric constants were measured with the apparatus described in the first two papers of this series,[1c,3] the dielectric constant of the benzene used in calibrating the condenser being taken as 2.279 at 25°. Measurements were made upon three heptanes of markedly different structure and upon the octane, 2,2,4-trimethylpentane, over the entire range of temperature within which they were liquid. The dielectric constants were measured at intervals of about 15° and the densities at intervals of about 20°. As the temperatures were not the same for different

[3] Smyth, Morgan and Boyce, THIS JOURNAL, **50**, 1536 (1928).

TABLE I

REFRACTIVE INDICES AND MOLAR REFRACTIONS AT 20°

	n_γ	n_β	n_D	n_α	MR_γ	MR_β	MR_D	MR_α
2,2-Dimethylpentane	1.39106	1.38710	1.38233	1.38038	35.32	35.00	34.61	34.46
2,4-Dimethylpentane	1.39097	1.38702	1.38233	1.38042	35.27	34.95	34.57	34.42
2-Methylhexane	1.39377	1.38983	1.38509	1.38311	35.26	34.95	34.57	34.41
n-Heptane	1.39646	1.39248	1.38777	1.38579	35.23	34.91	34.54	34.39
3-Methylhexane	1.39744	1.39343	1.38873	1.38677	35.13	34.82	34.45	34.30
2,2,3-Trimethylbutane	1.39817	1.39419	1.38940	1.38744	35.08	34.77	34.39	34.24
3,3-Dimethylpentane	1.39987	1.39589	1.39114	1.38918	35.00	34.69	34.32	34.17
2,3-Dimethylpentane	1.40071	1.39675	1.39201	1.39005	34.98	34.67	34.31	34.15
3-Ethylpentane	1.40232	1.39839	1.39366	1.39169	34.92	34.61	34.25	34.10
2,2,4-Trimethylpentane	1.40074	1.39649	1.39163	1.38962	40.07	39.69	39.25	39.08

measurements and as the values varied uniformly with temperature, the data were interpolated at 10° temperature intervals. These results for the dielectric constant and density, together with the values of the molar po-

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS OF THREE HEPTANES

	n-Heptane			2,2-Dimethylpentane			3-Ethylpentane		
t, °C.	ε	*d*	*P*	ε	*d*	*P*	ε	*d*	*P*
−120	...	...	...	2.120	0.7926	34.32	...	...	...
110	...	...	...	2.106	.7841	34.40	2.132	0.8079	33.95
100	...	...	...	2.091	.7757	34.42	2.118	.7995	34.00
90	2.083	0.7752	34.25	2.076	.7670	34.48	2.102	.7912	34.00
80	2.069	.7670	34.27	2.062	.7588	34.51	2.089	.7831	34.05
70	2.055	.7587	34.31	2.047	.7502	34.53	2.075	.7749	34.08
60	2.041	.7501	34.38	2.033	.7418	34.57	2.060	.7666	34.10
50	2.027	.7420	34.41	2.018	.7333	34.59	2.045	.7582	34.11
40	2.013	.7337	34.44	2.004	.7249	34.62	2.029	.7499	34.10
30	1.999	.7252	34.48	1.989	.7162	34.64	2.014	.7419	34.09
20	1.986	.7170	34.53	1.975	.7077	34.68	2.000	.7335	34.12
−10	1.972	.7088	34.55	1.960	.6993	34.70	1.985	.7251	34.13
0	1.958	.7004	34.60	1.945	.6908	34.72	1.971	.7160	34.19
+10	1.944	.6921	34.62	1.930	.6823	34.73	1.956	.7075	34.20
20	1.930	.6838	34.64	1.915	.6738	34.73	1.942	.6988	34.24
30	1.916	.6755	34.65	1.901	.6652	34.76	1.927	.6900	34.26
40	1.903	.6667	34.72	1.887	.6564	34.79	1.913	.6812	34.30
50	1.888	.6575	34.78	1.872	.6477	34.81	1.899	.6724	34.34
60	1.873	.6483	34.80	1.857	.6390	34.82	1.885	.6634	34.38
70	1.858	.6392	34.84	1.843	.6301	34.86	1.870	.6540	34.42
80	1.842	.6300	34.83	1.828	.6215	34.85	1.855	.6442	34.47
+90	1.825	.6208	34.79	...	...	...	1.840	.6340	34.55

TABLE III

DIELECTRIC CONSTANTS, DENSITIES, AND POLARIZATIONS OF 2,2,4-TRIMETHYLPENTANE

t, °C.	ϵ	d	P	t, °C.	ϵ	d	P
−100	2.114	0.7897	39.14	0	1.971	0.7078	39.42
90	2.100	.7814	39.19	+10	1.957	.6998	39.43
80	2.086	.7733	39.23	20	1.943	.6918	39.44
70	2.072	.7652	39.27	30	1.928	.6837	39.44
60	2.058	.7569	39.31	40	1.914	.6756	39.45
50	2.043	.7488	39.32	50	1.900	.6676	39.46
40	2.029	.7407	39.34	60	1.886	.6587	39.53
30	2.015	.7326	39.37	70	1.872	.6498	39.58
20	2.000	.7242	39.41	80	1.858	.6402	39.66
−10	1.985	.7160	39.40	90	1.844	.6303	39.76
				100	1.830	.6206	39.86

TABLE IV

PHYSICAL CONSTANTS OF THE HEPTANES AND OF 2,2,4-TRIMETHYLPENTANE AT 20°

	ϵ	$\frac{d\epsilon}{dT} \times 10^4 (20\text{–}30°)$	d	P	P_E	P_A	$MR_\gamma - MR_\alpha$	$n_\lambda - n_\alpha$	η
2,2-Dimethylpentane	1.915	14	0.6737	34.73	33.82	0.91	0.86	0.01068	0.00385
2,4-Dimethylpentane	1.917	15	.6745[a]	34.75	33.79	.96	.85	.01055	.00361
2-Methylhexane	1.922	14	.6789[a]	34.70	33.78	.92	.85	.01066	.00378
n-Heptane	1.930	14	.6836	34.65	33.77	.88	.84	.01067	.00409
3-Methylhexane	1.930	14	.6870[a]	34.49	33.68	.83	.83	.01067	.00372
2,2,3-Trimethylbutane	1.930	13	.6892	34.38	33.61	.78	.84	.01073	.00585
3,3-Dimethylpentane	1.940	15	.6934	34.45	33.55	.90	.83	.01069	.00454
2,3-Dimethylpentane	1.942	15	.6951[a]	34.42	33.54	.88	.83	.01066	.00406
3-Ethylpentane	1.942	15	.6988	34.24	33.48	.76	.82	.01063	.00377
2,2,4-Trimethylpentane	1.943	15	.6918	39.44	38.35	1.09	.99	.01112	.00503

[a] Determined by Dr. Graham Edgar.

larization calculated from them, are given in Tables II and III. Since the three heptanes and the octane showed similarity of behavior in their slight variation of the polarization with temperature as represented in Fig. 1, the other heptanes were measured only at 20 and 30°. For the sake of comparison, Table IV gives for each of the heptanes and for the 2,2,4-trimethylpentane at 20°, the dielectric constant, the temperature coefficient of the dielectric constant calculated from the values at 20° and 30°, the density, the molar polarization, P, and the molar refraction for light of infinite wave length $= P_E$. The values of P_A are calculated as $P - P_E$, which will be discussed later. The densities of all the heptanes at 20 and 30° have been determined by Dr. Graham Edgar. As the values which we have obtained at these temperatures are in excellent agreement with those of Dr. Edgar, we have used his values for four of the substances as indicated. The viscosities in c.g.s. units at 20°, measured by Mr. H. E. Rogers with a Bingham viscometer, as well as the dispersions calculated from the data in Table I, are included.

In Fig. 1 the scale on which the polarization is plotted against temperature is so large that many of the points appear to lie some distance from the straight lines which best represent them. Actually, the polarization of these substances varies little with temperature, but the variation, such as it is, is an approximately linear increase with increasing temperature, while,

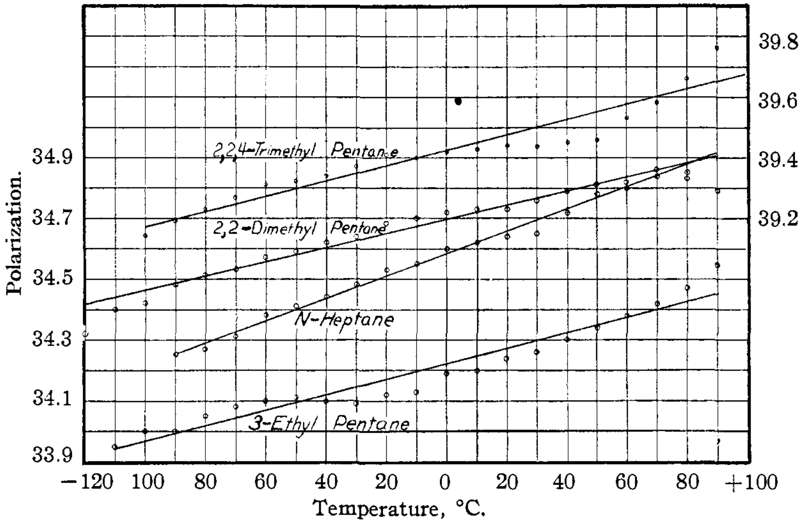

Fig. 1.—Variation of polarization with temperature. The values for the polarization of 2,2,4-trimethylpentane are shown at the right.

if the molecules possessed electric moments, the polarization would normally decrease with rising temperature. The increase, less than 2% for a 200° change of temperature, is not predicted by the theory of dielectric constants. As a small increase in refraction with rising temperature has been observed for a number of liquids, while vaporization also appears to bring about a slight increase in refraction,[4] it seems possible that the force fields of adjacent molecules reduce the mobilities of the bound electrons to a small extent, thereby reducing the refraction. As the molecular separation and motion increase with rising temperature, the effect of the force fields upon the electrons is decreased, the refraction, and hence the

[4] (a) Eisenlohr, "Spektrochemie organischer Verbindungen," F. Enke, Stuttgart, **1912**, p. 19; (b) Lorenz, *Ann. Physik*, **11**, 70 (1880); (c) Brühl, *Z. physik. Chem.*, **7**, 1 (1891).

polarization, thus being increased. Another and perhaps more important factor is the increase in the number of degrees of freedom with increasing temperature, which should facilitate the displacement of charges in the molecules and, hence, increase the polarization. As change of temperature alters the degree of molecular association or orientation, which has a great effect upon the polarization, the small effects just described may often be so masked as not to be apparent. Hexane, benzene and a few other substances which have electrically symmetrical molecules also show a slight increase in polarization with rising temperature.[1c,5]

The curves in Fig. 1 may be regarded as establishing the absence of any measurable electric moment in the molecules of the four substances represented. Consequently, $P_M = 0$ and $P_A = P - P_E$. As $P - P_E$ is practically the same for the other heptanes as for these which have no moment, it may be concluded that $P_M = 0$ for them also, that is, that they have no moments. Indeed, if P_A were neglected entirely and P_M set equal to $P - P_E$, the moments calculated would be exceedingly small. The conclusion is, therefore, justified that the moments of all the heptanes and of 2,2,4-trimethylpentane are zero or, at least, too small to be detected by any method now available, which, of course, is all that can be said as to the electric symmetry of any molecule.

In Tables I and IV the isomers are arranged in the order in which many of their properties have been found by Edgar and Calingaert[6] to fall. As would be expected, the dielectric constants, densities and refractive indices vary concomitantly. The temperature coefficients of the dielectric constants between 20 and 30° are approximately the same, but the data of Table II show that the coefficients over a wide range of temperature differ slightly from one another. The viscosities show a much greater variation in values than do any of the other properties listed and the first five in the list depart markedly from the regular order observed, at least approximately, for the other properties. The values of the dispersion, $n_\gamma - n_\alpha$, are approximately the same for all the heptanes, a marked rise being apparent on passing to the octane. The values of the molar dispersion, $MR_\gamma - MR_\alpha$, vary little, if any, more than might be caused by experimental error, but there appears to be a slight decrease in going down the list. A slight and irregular decrease is also apparent in going down the column of P_A values for the heptanes. The absolute variation in the values of P_A is much less than that in the values of P and P_E, which fall approximately in the usual order and vary concomitantly. As the refraction and polarization depend upon the mobility of the outer electrons of the molecule, the small but concomitant variations of P and P_E show that variation in the positions of the atoms in the molecules has a detectable effect

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[5] Isnardi, *Z. Physik*, **9**, 153 (1922); Sänger, *Physik. Z.*, **27**, 165 (1926).

[6] Private communication to the authors.

upon the mobilities of the binding electrons, the average mobility decreasing slightly in the order indicated by the decreasing values of P and P_E.

The conclusion to be drawn from these results, taken in conjunction with the work on other hydrocarbons, is that the atoms in a saturated hydrocarbon molecule may be joined together in every possible configuration without giving rise to any measurable lack of electric symmetry. This has a very definite bearing upon the electronic theories of valence in organic compounds, for the heptane molecules may be resolved into the various alkyl radicals to which it is customary to assign varying degrees of electronegativity, the formulas of the radicals being represented with a pair of bonding electrons at varying distances from their carbon atom.[7] If such a variation is an inherent property of the radicals, it should exist when the radicals occur in the heptane molecules and give rise to electric moments of varying sizes and, hence, to different values of P_M. It has been concluded that P_M differs from zero by a negligible amount. If it is not actually zero, any variation in its value must be included in that of P_A as calculated. The largest difference observed between the values of P_A for any two isomers, namely, that of 0.20 between 2,4-dimethylpentane and 3-ethylpentane, would, if due to but one pair of electrons, correspond to a displacement of the effective position of the charges of less than 3×10^{-11} cm. from a symmetrical location. It seems improbable that such a displacement and the very small change in forces which it must cause would have an appreciable effect upon the properties of the molecule. It must be further remembered that the possible displacement which has been estimated is the greatest that could occur and is probably much larger than any actually existing in these molecules. This does not preclude the possibility that the bonding electron pairs of different alkyl groups may be differently affected when they hold more polar groups in combination, but the relatively small variation in the electric moment of the molecule among the different alcohols and among the members of other series provides strong evidence[8] against the assumption of any considerable variation in the position of the bonding electron pair. The hypothesis of a bonding electron pair located in positions of varying unsymmetry thus receives no support from the physical evidence here considered.

Summary

The dielectric constants, densities, refractive indices, dispersions and viscosities of the isomers of heptane and of 2,2,4-trimethylpentane have been measured. The polarizations of three of the heptanes and of the octane calculated from dielectric constant and density measurements over

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[7] See Kharasch and Grafflin, This Journal, **47**, 1948 (1925); Kharasch and Marker, *ibid.*, **48**, 3130 (1926); Kharasch, *J. Chem. Education*, **5**, 404 (1928).

[8] Smyth, This Journal, **46**, 2151 (1924); Krchma and Williams, *ibid.*, **49**, 2408 (1927).

the entire range of temperature within which the substances are liquid increase very slightly with temperature, indicating that the molecules contain no electric moments. The very small differences between the polarizations and the molar refractions extrapolated to infinite wave length for all of the substances show the absence of a measurable moment in their molecules. It is concluded that the atoms in a saturated hydrocarbon molecule may be joined together in every possible configuration without giving rise to any measurable lack of electric symmetry, although very small differences in the rigidity of binding of the electrons are detected. The electrical symmetry of the molecules gives no evidence of a difference in the electronegativities of the various constituent radicals.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

SOLUTIONS OF SALTS IN PURE ACETIC ACID. I. PRELIMINARY PAPER[1]

BY ARTHUR W. DAVIDSON

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Introduction

The study of the solubilities and chemical reactions of salts in non-aqueous solvents reveals certain analogies between these solutions and the more familiar solutions in water. These analogies have been most extensively developed, by the well-known researches of Franklin and his co-workers, for solutions in liquid ammonia. Despite the large amount of work that has been done with other non-aqueous solvents, our knowledge of such solutions is still so fragmentary that the accumulation and organization of much additional information would seem to be desirable.

In a previous paper,[2] the writer described an attempt to study the solubilities and reactions of salts in anhydrous sulfuric acid, a liquid of very different nature from those non-aqueous solvents which have been most widely examined. It was found that the range of investigation in this solvent was severely limited by the fact that, due to the large self-ionization of sulfuric acid, reactions of a solvolytic nature were of such general occurrence as greatly to interfere with the study of other reactions. It was decided to investigate, from the same point of view, solutions of salts in anhydrous acetic acid, this liquid being sufficiently polar in nature to be a fairly good solvent for many salts, while its self-ionization is apparently very small, since its specific conductivity is of the order of 2×10^{-8} reciprocal ohm.

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the St. Louis meeting, April, 1928.

[2] Davidson, THIS JOURNAL, **47**, 968 (1925).