

The experimental data are reproduced by this equation with an average deviation of 0.5° .

TABLE II

Cpd.	$\Delta t_{\text{obs.}}$	Δw	Δp	$\Delta t_{\text{calcd.}}$	Dev.
<i>n</i> -Butane	0.0	0	0	0.0	0.0
2-Methylpropane	11.2	1	1	11.6	-.4
<i>n</i> -Pentane	0.0	0	0	0.0	.0
2-Methylbutane	8.2	2	0	7.9	.3
2,2-Dimethylpropane	26.6	4	2	26.7	-.1
<i>n</i> -Hexane	0.0	0	0	0.0	.0
2-Methylpentane	8.5	3	0	8.2	.3
3-Methylpentane	5.4	4	-1	5.4	.0
2,2-Dimethylbutane	19.0	7	0	19.0	.0
2,3-Dimethylbutane	10.8	6	-1	10.8	.0
<i>n</i> -Heptane	0.0	0	0	0.0	.0
2-Methylhexane	8.4	4	0	8.0	.4
3-Methylhexane	6.5	6	-1	6.5	.0
3-Ethylpentane	5.0	8	-2	5.0	.0
2,2-Dimethylpentane	19.2	10	0	20.0	-.8
2,3-Dimethylpentane	8.7	10	-2	9.0	-.3
2,4-Dimethylpentane	17.9	8	0	16.0	1.9
3,3-Dimethylpentane	12.4	12	-2	13.0	-0.6
2,2,3-Trimethylbutane	17.5	14	-2	17.0	.5
<i>n</i> -Octane	0.0	0	0	0.0	.0
2-Methylheptane	8.0	5	0	7.7	.3
3-Methylheptane	6.7	8	-1	6.7	.0
4-Methylheptane	8.0	9	-1	8.2	-.2
3-Ethylhexane	7.1	12	-2	7.3	-.2
2,2-Dimethylhexane	18.8	13	0	19.9	-1.1
2,3-Dimethylhexane	10.1	14	-2	10.4	-0.3
2,4-Dimethylhexane	16.2	13	-1	14.4	1.8
2,5-Dimethylhexane	16.6	10	0	15.3	1.3
3,3-Dimethylhexane	13.7	17	-2	15.0	-1.3
3,4-Dimethylhexane	8.0	16	-3	8.0	0.0
2-Methyl-3-ethylpentane	10.0	17	-3	9.5	.5
3-Methyl-3-ethylpentane	7.4	20	-4	8.6	-1.2
2,2,3-Trimethylpentane	15.8	21	-3	15.7	0.1
2,2,4-Trimethylpentane	26.4	18	0	27.5	-1.1
2,3,3-Trimethylpentane	10.9	22	-4	11.6	-0.7
2,3,4-Trimethylpentane	12.2	19	-3	12.5	-.3
2,2,3,3-Tetramethylbutane	19.4	26	-4	17.8	1.6

Average deviation 0.47°

In Table III, the method is extended to the boiling point data available for the nonanes and the decanes. The observed boiling point values for the nonanes comprise the complete set of values for the thirty-five nonanes given in A.P.I. Table 4a,³ omitting values for six compounds which were not based upon experimental data.⁵ The observed boiling points of the decanes represent individual determinations, obtained from the compilations of Egloff,⁶ Doss⁷ and Francis.⁸

The average deviations are 1.26° for twenty-nine nonanes, and 1.30° for twenty-eight decanes.

(5) Communication from Dr. Frederick D. Rossini.

(6) Egloff, "Physical Constants of the Hydrocarbons." Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939.

(7) Doss, "Physical Constants of the Principal Hydrocarbons," Fourth Edition, Texas Company, New York, N. Y., 1943.

(8) Francis, *Ind. Eng. Chem.*, **35**, 442 (1943).

TABLE III

Cpd.	$t_{\text{obs.}}$	Δw	Δp	$t_{\text{calcd.}}$	Dev.
<i>n</i> -Nonane	150.8	0	0	150.8	0.0
2-Methyloctane	143.3	6	0	143.5	.2
3-Methyloctane	144.2	10	-1	144.2	.0
4-Methyloctane	142.5	12	-1	141.8	-.7
3-Ethylheptane	143.0	.16	-2	142.5	-.5
4-Ethylheptane	141.2	18	-2	140.0	-1.2
2,2-Dimethylheptane	130.5	16	0	131.4	0.9
2,3-Dimethylheptane	140.5	18	-2	140.0	-.5
2,4-Dimethylheptane	133	18	-1	134.5	1.5
2,5-Dimethylheptane	136	16	-1	136.9	0.9
2,6-Dimethylheptane	135.2	12	0	136.3	1.1
3,3-Dimethylheptane	137.3	22	-2	135.2	-2.1
3,4-Dimethylheptane	140.5	22	-3	140.7	0.2
3,5-Dimethylheptane	20	-2		137.6	
4,4-Dimethylheptane	24	-2		132.8	
2-Methyl-3-ethylhexane	139	24	-3	138.3	-.7
2-Methyl-4-ethylhexane	22	-2		135.2	
3-Methyl-3-ethylhexane	28	-4		139.0	
3-Methyl-4-ethylhexane	26	-4		141.4	
2,2,3-Trimethylhexane	133.4	28	-3	133.4	.0
2,2,4-Trimethylhexane	126.5	26	-1	124.8	-1.7
2,2,5-Trimethylhexane	124.1	22	0	124.2	0.1
2,3,3-Trimethylhexane	138	30	-4	136.5	-1.5
2,3,4-Trimethylhexane	28	-4		139.0	
2,3,5-Trimethylhexane	131.4	24	-2	132.8	1.4
2,4,4-Trimethylhexane	131	28	-2	127.9	-3.1
3,3,4-Trimethylhexane	139	32	-5	139.6	0.6
3,3,5-Trimethylhexane	146.5	32	-6	145.1	-1.4
2,2-Dimethyl-3-ethylpentane	133.8	32	-4	134.1	0.3
2,3-Dimethyl-3-ethylpentane	142	34	-6	142.7	.7
2,4-Dimethyl-3-ethylpentane	136.7	30	-4	136.5	-.2
2,2,3,3-Tetramethylpentane	140.2	38	-6	137.8	-2.4
2,2,3,4-Tetramethylpentane	133.0	34	-4	131.7	-1.3
2,2,4,4-Tetramethylpentane	122.3	32	0	112.1	-10.2
2,3,3,4-Tetramethylpentane	141.5	36	-6	140.2	-1.3
<i>n</i> -Decane	174.0	0	0	174.0	0.0
2-Methylnonane	166.8	7	0	167.1	.3
3-Methylnonane	167.8	12	-1	167.7	-.1
4-Methylnonane	165.7	15	-1	164.8	-.9
5-Methylnonane	165.1	16	-1	163.8	-1.3
2,4-Dimethyloctane	153.2	23	-1	157.0	3.8
2,5-Dimethyloctane	159	22	-1	157.9	-1.1
2,6-Dimethyloctane	160	19	-1	160.9	0.9
2,7-Dimethyloctane	160.2	14	0	160.3	.1
3,3-Dimethyloctane	161.2	27	-2	158.5	-2.7
3,6-Dimethyloctane	160.8	24	-2	161.5	0.7
4,5-Dimethyloctane	161.0	30	-3	161.1	.1
4- <i>n</i> -Propylheptane	161.7	27	-2	158.5	-3.2
4-Isopropylheptane	158.6	34	-3	157.2	-1.4
2-Methyl-5-ethylheptane	158.4	27	-2	158.5	0.1
3-Methyl-3-ethylheptane	156.3	36	-4	160.7	4.4
2,2,4-Trimethylheptane	147	34	-1	146.2	-0.8
2,2,5-Trimethylheptane	148.9	26	0	148.5	-.4
2,3,3-Trimethylheptane	160	38	-4	158.8	-1.2
2,3,6-Trimethylheptane	155.3	29	-2	156.6	1.3
2,4,4-Trimethylheptane	151	38	-2	147.8	-3.2
2,4,6-Trimethylheptane	147.6	30	-1	150.1	2.5
2,5,5-Trimethylheptane	152.8	34	-2	151.7	-1.1
3,4-Diethylhexane	160.7	40	-5	162.3	1.6
2,2-Dimethyl-4-ethylhexane	148	39	-2	146.8	-1.2
2,2,3,4-Tetramethylhexane	156.5	47	-5	155.4	-1.1
2,2,4,5-Tetramethylhexane	145.8	41	-2	144.8	-1.0
2,2,5,5-Tetramethylhexane	136.8	38	0	136.8	0.0

The average deviation for all ninety-four compounds is 0.97° .⁹

For the nonanes, a complete set of predicted boiling points is given in Table III. Table IV lists the predicted boiling points for the 47 decanes which do not appear in Table III.

(9) These average deviations were obtained disregarding sign; considering sign, the average deviation for the 94 compounds is -0.27° .

TABLE IV

Cpd.	Δw	Δp	$t_{\text{calcd.}}$
3-Ethyl-octane	20	-2	165.4
4-Ethyl-octane	24	-2	161.5
2,2-Dimethyl-octane	19	0	155.4
2,3-Dimethyl-octane	22	-2	163.4
3,1-Dimethyl-octane	28	-3	163.1
3,5-Dimethyl-octane	27	-2	158.5
4,4-Dimethyl-octane	31	-2	154.6
2-Methyl-3-ethylheptane	31	-3	160.1
2-Methyl-4-ethylheptane	31	-2	154.6
3-Methyl-4-ethylheptane	36	-4	160.7
3-Methyl-5-ethylheptane	32	-3	159.1
4-Methyl-3-ethylheptane	35	-4	161.7
4-Methyl-4-ethylheptane	39	-4	157.8
2,2,3-Trimethylheptane	35	-3	156.2
2,2,5-Trimethylheptane	31	-1	149.1
2,3,4-Trimethylheptane	37	-4	159.7
2,3,5-Trimethylheptane	34	-3	157.2
2,4,5-Trimethylheptane	35	-3	156.2
3,3,4-Trimethylheptane	42	-5	160.3
3,3,5-Trimethylheptane	39	-3	152.3
3,4,4-Trimethylheptane	43	-5	159.4
3,4,5-Trimethylheptane	40	-5	162.3
2-Methyl-3-isopropylhexane	41	-4	155.8
3,3-Diethylhexane	44	-6	163.9
2,2-Dimethyl-3-ethylhexane	43	-4	153.9
2,3-Dimethyl-3-ethylhexane	46	-6	161.9
2,3-Dimethyl-4-ethylhexane	42	-5	160.3
2,4-Dimethyl-3-ethylhexane	43	-5	159.4
2,4-Dimethyl-4-ethylhexane	43	-4	153.9
2,5-Dimethyl-3-ethylhexane	38	-3	153.3
3,3-Dimethyl-4-ethylhexane	47	-6	160.9
3,4-Dimethyl-3-ethylhexane	48	-7	165.5
2,2,3,3-Tetramethylhexane	50	-6	158.0
2,2,3,5-Tetramethylhexane	42	-3	149.3
2,2,4,4-Tetramethylhexane	46	-2	139.9
2,3,3,4-Tetramethylhexane	50	-7	163.5
2,3,3,5-Tetramethylhexane	45	-4	151.9
2,3,4,4-Tetramethylhexane	49	-6	159.0
2,3,4,5-Tetramethylhexane	44	-5	158.4
3,3,4,4-Tetramethylhexane	54	-8	165.1
2,4-Dimethyl-3-isopropylpentane	48	-5	154.5
2-Methyl-3,3-diethylpentane	51	-8	168.0
2,2,3-Trimethyl-3-ethylpentane	55	-8	164.1
2,2,4-Trimethyl-3-ethylpentane	50	-5	152.5
2,3,4-Trimethyl-3-ethylpentane	53	-8	166.1
2,2,3,3,4-Pentamethylpentane	57	-8	162.1
2,2,3,4,4-Pentamethylpentane	54	-5	148.6

The path number w was calculated as the total distance between all carbon atoms. The smaller this total distance, the larger is the compactness of the molecule. This means that as the compactness increases, *i.e.*, as w decreases, the boiling point decreases, as is shown by writing equation (1) in the form

$$t_B = \frac{98}{n^2} w + 5.5p + c \quad (7)$$

The boiling point is seen to vary inversely with compactness. Other factors being equal, the

frequency of molecular collisions will be less in the more compact of two isomers. As a result, the more compact isomer will require less heat to compensate for energy losses due to molecular collisions, and will therefore boil at a lower temperature. The factor $1/n^2$ before the compactness term indicates a damping effect of molecular weight.

The structural number p may be interpreted as a semi-quantitative measure of intramolecular attraction forces transmitted through the carbon chain. The theory of alternate polarities (Lapworth) can be extended to non-substituted paraffins, as was done by Cuy.¹⁰ If, then, alternate carbon atoms in a chain tend to exhibit opposite polarities, and if, for purposes of approximation, such charges are taken to be of equal magnitude, then the total inductive attraction force between atoms of opposite polarities is given by an expression of the form $k_1p_1 + k_3p_3 + k_5p_5 \dots$, where p_1 is the number of carbon atoms one bond apart, p_3 the number three apart, etc. Clearly, the numerical values of the coefficients k_1, k_3, k_5 , will decrease strongly in that order, as attraction forces will obey an inverse-power law. For any paraffin of n carbon atoms, $p_1 = n - 1$. The difference between the intramolecular attraction in two isomers reduces therefore to $k_3\Delta p_3 + k_5\Delta p_5$. As k_5 is small compared to k_3 , this is further simplified to $k_3\Delta p_3$. In equation (4), this term appears as $5.5\Delta p$.

The alternating irregularity frequently observed in physical and chemical properties of organic compounds may also be noted for the boiling points in a group of paraffin isomers. When a methyl group, for example, is displaced by single steps along a carbon chain, the boiling points of the resulting series of isomers oscillate strongly. As shown by the examples given below, this effect is closely reproduced by the calculated values. This phenomenon, therefore, may be traceable in part to the antagonistic effects of the compactness and of the polarity factors.

Series (a)	t_B obs.	t_B calcd.
	90.0	90.4
	80.5	82.4
	89.7	89.4
	79.2	78.4
	91.9	91.9

(10) Cuy, THIS JOURNAL, 42, 503 (1920).

Series (b)		
C—C—C—C—C—C—C—C	125.7	125.7
C—C—C—C—C—C—C	117.7	118.0
C		
C—C—C—C—C—C—C	119.0	119.0
C		
C—C—C—C—C—C—C	117.7	117.5
C		

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Summary

The boiling points of the paraffins may be correlated with structure by means of the equation $\Delta t = (98/n^2) \Delta w + 5.5 \Delta p$, where Δw and Δp are structural variables which provide simple numerical measures of the effect produced on all atoms simultaneously by a change in position of an atom or of a group. The average deviation between calculated and observed values is less than one degree for the 94 paraffins considered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Raman Spectra of Aqueous Solutions of Potassium Thiocyanate

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Introduction

The Raman spectrum of water, the most conspicuous example of molecular association in the liquid state, has been subjected to numerous studies, especially on the modification of the main band between $\Delta\bar{\nu}$ 3200–3600 cm^{-1} at different temperatures,¹ by the effect of solutes² and in the crystalline field.³ The presence of ions usually increases the intensity of Raman scattering, shifts the maxima and alters the relative intensities of band components, and is in general parallel to the effect of increased temperature. These effects have been explained as due to a gradual change of the water structure, pictured either as a change in a quasi-lattice arrangement of water molecules,^{1c} or as a dissociation of water polymers.^{1a} The temperature and solute effects on water structure have also been studied by X-ray diffraction,⁴ infrared absorption spectra,⁵ magnetic susceptibility measurements,⁶ and investigation of the thermodynamic properties of water and aqueous solutions of electrolytes. Recent calorimetric measurements⁷ have shown that the heat of vaporization of water from concentrated potassium thiocyanate solutions at 30° is about 2% lower than that from pure water. This indicates the breaking of hydrogen bonds of liquid water in the ionic field created by the solute. The Raman spectrum of potassium thiocyanate in aqueous

solution has previously been reported,⁸ but since no information on the modification of the Raman band of the water was included the present investigation was carried out.

Experimental Details

The 4358 Å. line of mercury was employed for excitation. Two experimental arrangements were used, one with six G.E. H-2 mercury vapor lamps and a horizontal Raman tube, the other with seven water cooled d. c. mercury arcs and a vertical Raman tube. The arcs⁹ were made of 10-mm. Pyrex tubing, gave an effective arc length of 9", and operated at 5–8 amperes at 80–90 volts. The water-cooled arcs gave lower light output, but relatively less background and yielded cleaner spectra. The filter solution¹⁰ used to isolate the λ 4358 Å. line consisted of 4% *p*-nitrotoluene and 1/10,000 crystal violet R B bluish, (Cassella Color Co.), in 95% ethyl alcohol.

The spectrograph used was a Steinheil type GH, with three glass prisms and f/3 195 mm. f.1. collimator and camera lenses. Spectra were taken on Eastman 103J plates, developed in D19, and then traced by a photoelectric microdensitometer. An iron arc comparison spectrum was taken on each plate and traced alongside the Raman spectrum. Displacements of peaks on the tracing were measured to within 0.03 mm. by means of a special comparator constructed by Mr. L. K. Henke, laboratory chief mechanician, and frequencies were determined by linear interpolation of the wave numbers of the two nearest iron lines. Rayleigh scattering of the mercury λ 4916 or λ 4078 Å. line was used for correction of any lateral displacement between the Raman and comparison spectra occurring either during picture taking or during tracing. All wave numbers were reduced to those in vacuum by means of Kayser's table.¹¹

Solutions were prepared from reagent potassium thiocyanate and conductivity water. Controlled exposures ranging from two minutes to two hours were used, at a

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(9) The author is indebted to Dr. Paul Bender and Messrs. Philip Lyons and Paul Reinker for the development of the arcs used in this work.

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