[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE]

Structural Determination of Paraffin Boiling Points

By HARRY WIENER¹

The boiling points of organic compounds, as well as all their physical properties, depend functionally upon the number, kind and structural arrangement of the atoms in the molecule. Within a group of isomers, both the number and the kind of atoms are constant, and variations in physical properties are due to changes in structural interrelationships alone. The study of the effect of pure structural variation upon the boiling point of the paraffins may be expected to be of some theoretical interest. It will be shown in this paper that satisfactory results can readily be obtained by this approach.

The boiling points of the paraffins are given by the linear formula

$$t_{\rm B} = aw + bp + c \tag{1}$$

where a, b and c are constants for a given isomeric group, and p and w are structural variables defined below.

The polarity number p is defined as the number of pairs of carbon atoms which are separated by three carbon-carbon bonds. *E.g.*, for 2,3-dimethylpentane

The path number w is defined as the sum of the distances between any two carbon atoms in the molecule, in terms of carbon-carbon bonds. Brief method of calculation: Multiply the number of carbon atoms on one side of any bond by those on the other side; w is the sum of these values for all bonds. *E.g.*, for 2-methylbutane

The problem is simplified by a change in notation already employed in this connection by Taylor, Pignocco and Rossini.² Let t_0 be the boiling point of the straight-chain member of the group of isomers, having structural variables w_0 and p_0 , and let $\Delta t = t_0 - t_B$, $\Delta w = w_0 - w$, $\Delta p = p_0 - p$. Then, for an isomer with structural variables w and p, equation (1) becomes

$$\Delta t = a \,\Delta w + b \,\Delta p \tag{2}$$

Equation (2) was extended to cover the entire paraffin series. For a compound with n carbon atoms, the following relation was found to hold

$$\Delta t = \frac{k}{n^2} \,\Delta w + b \,\Delta p \tag{3}$$

Equation (3) was fitted, by means of the method

Present address: 5120 19th-Avenue, Brooklyn 4, N. Y.
 Taylor, Pignocco and Rossini, J. Research Bur. Standards, 34, 413 (1945).

of least squares, to the selected boiling point data for the thirty-seven paraffins from C_4H_{10} to C_8H_{18} in the tables of the American Petroleum Institute Research Project 44.³

The resulting equation is

$$\Delta t = \frac{98}{n^2} \Delta w + 5.5 \Delta p \tag{4}$$

which is the form used in this paper.

The change in notation introduced by equation (2) is useful not only because of the resulting simplification, but also because it refers the boiling points of the branched isomers to the boiling points of the normal paraffins, which throughout the series have been much more intensively and accurately determined and correlated. In particular, Egloff's equation⁴:

$$t_0 = 745.42 \log (n + 4.4) - 689.4 \tag{5}$$

reproduces the data to within their experimental limits. Table I gives the reference values for the normal paraffins from *n*-butane to *n*-dodecane. For normal paraffins, the structural variables are given by

$$w_0 = \frac{1}{6} (n-1)(n)(n+1), \quad p_0 = n-3 \quad (6)$$

Table I

NORMAL PARAFFINS

÷.	Olding T THEFT	****	
Cpd.	to	wo	⊅ 0 _
<i>n</i> -Butane	-0.5	10	1
<i>n</i> -Pentane	36.1	20	2
<i>n</i> -Hexane	68.7	35	3
<i>n</i> -Heptañe	98.4	56	4
<i>n</i> -Octane	125.7	84	$\overline{5}$
<i>n</i> -Nonane	150.8	120	6
<i>n</i> -Decane	174.0	165	7
n-Undecane	195.8	220	8
n-Dodecane	216.2	286	9

Example of calculation:

3-Ethylhexane
$$w = 72, \Delta w = 12, p = 7, \Delta p = C - C - C - C - C - C - C - 2, \Delta t_{calcd.} = 7.3^{\circ}, \Delta t_{obs.} = 7.1^{\circ}, Deviation = -0.2^{\circ}, Calcd. C b. p.: $tB = t_0 - \Delta t = 125.7 - 7.3 = 118.4^{\circ}$$$

Table II lists the detailed results obtained by applying equation (4) to the thirty-seven paraffins from C_4H_{10} to C_8H_{18} , for which carefully selected boiling point values are given in the A.P.I. tables,³ and from which data the two empirical constants of equation (4) were evaluated.

⁽³⁾ American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected values of Physical and Thermodynamical Properties of Hydrocarbons. Tables No. 1a, 2a, 3a and 4a, dated June 30, 1945.

⁽⁴⁾ Egloff, Sherman and Dull, J. Phys. Chem., 44, 730 (1940).

TABLE III

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

, • • •, •		•	. *		2	•					-
equation with an aver	rage de	eviat	tion c	of 0.5° .	,	Cpd.	tubs.	Δw	Δp	fealed.	Dev.
	TABLE	TT				n-Nonane	150.8	0	0	150.8	0.0
				•		2-Methyloctane	143.3	6	0	143.5	.2
Cpd.	Δt_{obs} .	Δw	∆⊅	$\Delta t_{\text{caled.}}$	Dev.	3-Methyloctane	144.2	10	-1	144.2	.0
<i>n</i> -Butane	0.0	0	0	0.0	0.0	4-Methyloctane 3-Ethylheptane	$142.5 \\ 143.0$	$12 \\ .16$	$-1 \\ -2$	141.8	7
2-Methylpropane	11.2	1	1	11.6	4	4-Ethylheptane	143.0 141.2	18	-2 -2	142.5 140.0	5 -1.2
<i>n</i> -Pentane	0.0	0	0	0.0	.0	2,2-Dimethylheptane	130.5	16	-2	131.4	0.9
2-Methylbutane	8.2	2	0	7.9	.3	2,3-Dimethylheptane	140.5	18	-2^{-2}	140.0	5
2,2-Dimethylpropane	26.6	4	$\overset{\circ}{2}$	26.7	1	2,4-Dimethylheptane	133	18	-1	134.5	1.5
<i>n</i> -Hexane	0.0	0	õ	0.0		2,5-Dimethylheptane	136	16	-1	136.9	0.9
					.0	2,6-Dimethylheptane	135.2	12	0	136.3	1.1
2-Methylpentane	8.5	3	0	8.2	.3	3,3-Dimethylheptane	137.3	22	-2	135.2	-2.1
3-Methylpentane	5.4	4	-1	5.4	.0	3,4-Dimethylheptane 3,5-Dimethylheptane	140.5	$\frac{22}{20}$	-3 -2	$140.7 \\ 137.6$	0.2
2,2-Dimethylbutane	19.0	7	0	19.0	.0	4,4-Dimethylheptane		24	$-\frac{2}{2}$	137.0 132.8	
2,3-Dimethylbutane	10.8	6	-1	10.8	.0	2-Methyl-3-ethylhexane	139	$\frac{24}{24}$	-3	138.3	7
<i>n</i> -Heptane	0.0	0	0	0.0	.0	2-Methyl-4-ethylhexane		22	-2	135.2	
2-Methylhexane	8.4	4	0	8.0	.4	3-Methyl-3-ethylhexane		28	-4	139.0	
3-Methylhexane	6.5	6	-1	6.5	.0	3-Methyl-4-ethylhexane		26	-4	141.4	
3-Ethylpentane	5.0	8	-2^{-1}	5.0	.0	2.2,3-Trimethylhexane	133.4	28	-3	133.4	.0
2,2-Dimethylpentane	19.2	10	0	20.0	8	2,2,4-Trimethylhexane	126.5	26	-1	124.8	-1.7
			-2^{0}			2,2,5-Trimethylhexane 2,3,3-Trimethylhexane	$124.1 \\ 138$	$\frac{22}{30}$	$^{0}_{-4}$	124.2 136.5	0.1 1.5
2,3-Dimethylpentane	8.7	10		9.0		2,3,4-Trimethylhexane	158	28^{-30}	-4	130.5 139.0	÷-1,5
2,4-Dimethylpentane	17.9	8	0	16.0	1.9	2,3,5-Trimethylhexane	131.4	24	-2	132.8	1.4
3,3-Dimethylpentane	12.4	12	-2	13.0	-0.6	2,4,4-Trimethylhexane	131	$\overline{28}$	-2	127.9	-3.1
2,2,3-Trimethylbutane	17.5	14	-2	17.0	.5	3,3,4-Trimethylhexane	139	32	5	139.6	0.6
n-Octane	0.0	0	0	0.0	.0	3,3-Diethylpentane	146.5	32	-6	145.1	-1.4
2-Methylheptane	8.0	5	0	7.7	.3	2,2-Dimethyl-3-ethylpentane		32	-4	134.1	0.3
3-Methylheptane	6.7	8	-1	6.7	.0		142	34	-6	142.7	.7
4-Methylheptane	8.0	9	-1	8.2	2	2,4-Dimethyl-3-ethylpentane 2,2,3,3-Tetramethylpentane	136.7 140.2	$\frac{30}{38}$	-4 - 6	136.5 137.8	2 -2.4
3-Ethylhexane	7.1	12	-2^{-1}	7.3	2	2,2,3,4-Tetramethylpentane	133.0	34	-4	137.3 131.7	-2.4 -1.3
2.2-Dimethylhexane	18.8	13	0	19.9	-1.1	2,2,4,4-Tetramethylpentane	122.3	32	ō	112.1	-10.2
						2,3,3,4-Tetramethylpentane	141.5	36	- 6	140.2	-1.3
2,3-Dimethylhexane	10.1	14	-2	10.4	-0.3	n-Decane	174.0	0	0	174.0	0.0
2,4-Dimethylhexane	16.2	13	-1	14.4	1.8	2-Methylnonane	166.8	7	0	167.1	.3
2,5-Dimethylhexane	16.6	10	0	15.3	1.3	3-Methylnonane	167.8	12	-1	167.7	1
3,3-Dimethylhexane	13.7	17	2	15.0	-1.3	4-Methylnonane	165.7	15	-1	164.8	9
3,4-Dimethylhexane	8.0	16	-3	8.0	0.0	5-Methylnonane 2,4-Dimethyloctane	$165.1 \\ 153.2$	$\frac{16}{23}$.	$-1 \\ -1$	$163.8 \\ 157.0$	$-1.3 \\ 3.8$
2-Methyl-3-ethylpentane	10.0	17	-3	9.5	.5	2,5-Dimethyloctane	159	$\frac{23}{22}$	-1	157.9	-1.1
3-Methyl-3-ethylpentane		20	-4	8.6	-1.2	2,6-Dimethyloctane	160	19	-1	160.9	0.9
2,2,3-Trimethylpentane	15.8	21	-3	15.7	0.1	2,7-Dimethyloctane	160.2	14	0	160.3	.1
2,2,4-Trimethylpentane	26.4	18	Ő	27.5	-1.1	3,3-Dimethyloctane	161.2	27	-2	158.5	-2.7
		$\frac{10}{22}$	-4	11.6	-0.7	3,6-Dimethyloctane	160.8	24	-2	161.5	0.7
2,3,3-Trimethylpentane	10.9					4,5-Dimethyloctane	161.0	30	-3	161.1	.1
2,3,4-Trimethylpentane	12.2	19	-3	12.5	→ 3	4-n-Propylheptane	161.7	27	-2	158.5	-3.2
2,2,3,3-Tetramethyl-						4-Isopropylheptane 2-Methyl-5-ethylheptane	$158.6 \\ 158.4$	$\frac{34}{27}$	$-3 \\ -2$	157.2 158.5	-1.4 0.1
butane	19.4	26	4	17.8	1.6	3-Methyl-3-ethylheptane	156.3	36	-4	160.7	4.4
		Δ.		J	0 479	2,2,4-Trimethylheptane	147	34	-1	146.2	-0.8
		Av	erage	ueviati	on 0.47°	2,2,6-Trimethylheptane	148.9	26	ō	148.5	4
In Table III, the	meth	i he	e evt	hahna	to the	2,3,3-Trimethylheptane	160	38	- 4	158.8	-1.2
boiling point data av						2,3,6-Trimethylheptane	155.3	29	-2	156.6	1.3
						2,4,4-Trimethylheptane	151	38	-2	147.8	3.2
the decanes. The ob	Jserve	u D(ming	point	. vaiues	2,4,6-Trimethylheptane	147.6	30 24	-1	150.1	2.5

boining 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 twentynine 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).

The average deviation for all ninety-four compounds is $0.97^{\circ.9}$

152.8

160.7

156.5

145.8

136.8

148

34

40 - 5

39 - 2

47

41

38

-2

-5

-2

0

151.7

162.3

146.8

155.4

144.8

136.8

--1.1

1.6

-1.2

-1.1

--1.0

0.0

2,3,5-Trimethylheptane

2,2-Dimethyl-4-ethylhexane

2,2,3,4-Tetramethylhexane

2,2,4,5-Tetramethylhexane

2,2,5,5-Tetramethylhexane

3,4-Diethylhexane

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	tcaled.				
3-Ethyloctane	20	-2	165.4				
4-Ethyloctane	$\overline{24}$	-2^{-2}	161.5				
2,2-Dimethyloctane	19	0	155.4				
2.3 Dimethyloctane	22	-2	163.4				
3,1 Dimethyloctane	28	-3	163.1				
3,5 Dimethyloctane	27	-2	158.5				
4,4-Dimethyloctane	31	-2^{-1}	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		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^{-1}	160.3				
3,3,5-Trimethylheptane	39	-3	152.3				
3,4,4-Trimethylheptane	43	-5	152.0 159.4				
3,4,5-Trimethylheptane	40	-5	162.3				
2-Methyl-3-isopropylhexane	41	<u>-4</u>	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-othylpeutane	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				

TADID IV

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

$$t_{\rm B} = \frac{98}{n^2} w + 5.5p + c \tag{7}$$

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 $k_1p_1 + k_3p_3 + k_5p_5 \cdots$, 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)

$$t_{B obs.}$$
 $t_{B caled.}$

 C--C--C--C--C
 90.0
 90.4

 C
 C
 C

$$C - C - C - C - C = C = 80.5 \quad 82.4$$

(10) Cuy, This Journal, 42, 503 (1920).

Series (b)		
С-С-С-С-С-С-С	125.7	125.7
CCCCC C	117.7	118.0
CCCCC C	119.0	119.0
C-C-C-C-C-C-C	117.7	117.5

fessor James Singer and to Miss Ann Palm for valuable assistance.

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

By JEN-YUAN CHIEN

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 $\Delta \tilde{\nu}$ 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

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(2) (a) J. H. Hibben, J. Chem. Phys., 5, 166 (1937); (b) P. A. Leighton and J. Burnham, THIS JOURNAL, 59, 424 (1937); (c) Th. G. Kujumzelis, Z. Physik, 110, 760 (1938).
(3) P. G. N. Nayar, "Raman Jubilee Volume," p. 419 (1938).

(4) (a) J. Morgan and B. E. Warren, J. Chem. Phys., 6, 666 (1938); (b) G. W. Stewart, ibid., 7, 869 (1939), 11, 72 (1943).

(5) E. Ganz, Ann. Physik, 28, 445 (1937).

(6) Cf. N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., 1940, p. 166.

(7) J. B. Hunter and H. Bliss, Ind. Eng. Chem., 36, 950 (1944)

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 10mm. 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 $\lambda 4916$ or $\lambda 4078$ 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

(8) (a) A. Dadieu and K. W. F. Kohlrausch, Monatsh., 55, 400 (1930). (b) P. Krishnamurti, Ind. J. Phys., 5, 663 (1930). A. Langseth, J. R. Nielsen and J. U. Sorensen, Z. physik. Chem., B27, 102 (1934). (d) J. Goubeau and O. Gott, Ber., 73, 127 (1940).

(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.

(10) B. Uribe-Vergara, Thesis, University of Wisconsin, 1945.

(11) H. Kayser, "Tabelle der Schwingungszahlen," Edwards Bros., Ann Arbor, Michigan, lithographic reprint, 1944.