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The Refractive Index of Paraffins in Terms of the Number and Frequency of the Dispersion Electrons[1]

BY S. S. KURTZ, JR., AND M. R. LIPKIN

This paper, which is part of a general investigation of the density and refractive index of hydrocarbons, is restricted to the refractive index and density of paraffin hydrocarbons, and the effect of temperature and pressure on these properties.

It has been shown in previously published work[2-4] that there is a direct relation between the number of the dispersion electrons, calculated using the Sellmeier–Drude equation, and the number of formula bonds in hydrocarbons. Calculations of this type indicate that all valence electrons in saturated hydrocarbons (in C–C or C–H bonds, and in straight or branched structures) have approximately the same effect in refracting light, *i. e.*, they have the same degree of harmonic coupling with the electromagnetic waves.

In this paper we make the approximation that all valence electrons in saturated hydrocarbons do have the same effect on the refraction of light, even though we recognize the fact that future work may make it necessary to distinguish between C–C and C–H bonds[4] (p. 714). There is also evidence of small secondary effects due to structure; for example, the normal compound always falls slightly above the line corresponding to the average Newton constant,[5] as shown in Fig. 1 of Kurtz and Ward[4] and Figs. 1, 2, and 3 of Ward and Kurtz.[6] However, these structural effects are small, and can reasonably be considered of a secondary order of importance.[7]

The point of view just given is fundamentally different from the molecular refraction point of view,[8] which focuses attention on the molecule as a whole, rather than on the individual valence bonds and the electrons which form these bonds. Molar polarity is a justifiable concept in considering the dielectric constant of polar molecules, since the whole molecule can orient in an electrostatic field. The portion of the dielectric constant not caused by molecular orientation is approximately equal to the square of the refractive index and, like the refractive index, can be attributed to the harmonic coupling between the valence electrons and the electromagnetic field. For non-polar compounds, therefore, it would appear desirable to focus attention on the valence electrons rather than on the molecule as a whole.

The properties of non-polar dielectrics have recently been considered from several divergent points of view.[9-15]

The present paper will not discuss or evaluate the cited literature. It is a field in which much experimental and theoretical work is needed.

In calculating the number and frequency of dispersion electrons for paraffins, Equation 1 has been used to obtain B and V_0.

$$n^2 - 1 = \frac{B}{V_0^2 - V^2} \qquad (1)$$

The values of n and V for the alpha and beta lines of hydrogen are introduced in Equation 1 which is then solved for B and V_0. The number of dispersion electrons per bond, k, is then calculated from B using Equation 2.

$$B = k\frac{db}{M}\frac{Ae^2}{\pi m_0} = k\frac{db}{M} \times 4.8861 \times 10^{31} \qquad (2)$$

When the temperature differs from 20°, or the pressure differs from 1 atmosphere, Equation 3 is used.

$$n^2 - 1 = \frac{B}{(V_0 + \phi)^2 - V^2} \qquad (3)$$

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[1] Presented before the Division of Physical Chemistry at the September, 1940, meeting of the American Chemical Society.

[2] (a) P. Drude, *Ann. Physik*, **14**, 677–725 (1904); (b) H. Erfle, *ibid.*, **24**, 672–708 (1907).

[3] H. Erfle, *Z. physik. Chem.*, **61**, 399–421 (1908).

[4] S. S. Kurtz, Jr., and A. L. Ward, *J. Franklin Inst.*, **224**, 583, 697 (1937).

[5] I. Newton, "Opticks," Book II, Part III, Edition of 1717, pp. 245–251.

[6] A. L. Ward and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **30**, 559 (1938).

[7] The relatively large structural effect calculated by Huggins (see ref. 19) results from the fact that the slope of the refractive index density function specified by the Gladstone and Dale equation is out of line with the data for groups of paraffin isomers.[4,6]

[8] (a) P. Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y., 1929; (b) F. Eisenlohr, "Spectrochemie organischer Verbindungen," F. Enke, Stuttgart, 1912.

[9] C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.* (London), **A117**, 589–599 (1928).

[10] S. S. Rao and M. Qureshi, *J. Osmania Univ.*, **5**, 20–6 (1937) [*C. A.*, **34**, 4955 (1940)].

[11] F. G. Keyes and J. G. Kirkwood, *Phys. Rev.*, **37**, 202–215 (1931).

[12] H. H. Uhlig, J. G. Kirkwood and F. G. Keyes, *J. Chem. Phys.*, **1**, 151 (1933).

[13] J. G. Kirkwood, *ibid.*, **4**, 592–601 (1936).

[14] C. G. Darwin, *Proc. Roy. Soc.* (London), **A146**, 17 (1934).

[15] A. O'Rahilly, "Electro-Magnetics," Longmans, Green and Co., New York, N. Y., 1938, pp. 456–9.

The ϕ coefficient in this equation was developed by Kurtz and Ward.[4] For saturated hydrocarbons, ϕ is given by Equation 4.

$$\phi = 0.47 \times 10^{15} (d^{20}{}_4 - d_{t,p}) \qquad (4)$$

The symbols used in these equations and in the balance of the paper are as follows

n = refractive index
ϵ = dielectric constant
V_0 = the frequency of the dispersion electrons in seconds^{-1}
V = the frequency of the light refracted = $\dfrac{2.9986 \times 10^{10} \text{ cm. sec.}^{-1}}{\text{wave length in cm.}}$
V^2 for H_α = 2.0876×10^{29}
V^2 for D = 2.5892×10^{29}
V^2 for H_β = 3.8053×10^{29}
B = constant characteristic of any one compound
ϕ = increment of frequency of the dispersion electrons which takes care of the effect of temperature or pressure
ψ = $(\Delta V_0/\Delta d)$ for the effect of temperature and pressure = 0.47×10^{15} for paraffins and naphthenes
b = formula bonds per molecule (either C–C or C–H)
k = the apparent number of dispersion electrons per formula bond
k normal paraffins = 1.0760
k average paraffins = 1.0710
d = density in g./ml.
$d_{t,p}$ = d at temperature t and pressure p
M = molecular weight, g./mole
A = Avogadro's constant = 6.061×10^{23}
e = charge of an electron = 4.774×10^{-10} e. s.
m_0 = mass of an electron = 8.999×10^{-28} g.
F = frequency constant in the equation relating V_0 to density for the paraffin homologous series. F = 3.2313 for normal paraffins or 3.2301 for average paraffins (see Equation 7)
h = Planck's constant = 6.547×10^{-27}
E = energy in ergs

Good data for the refractive index for the alpha and beta lines of hydrogen are needed if the solution of these equations is to be accurate. Fortunately, it is possible to calculate these values since the difference between these two refractive indices, divided by the density, is a constant for all saturated hydrocarbons.[6] For 48 paraffins and 45 naphthenes, the average value is 99×10^{-4}. The maximum difference between the average specific dispersion value 99×10^{-4} and the observed specific dispersion for groups of paraffin isomers corresponds to about 3 in the fourth decimal of the refractive index, which probably represents experimental error. There is no definite trend with increasing molecular weight.

Using the average value of 99×10^{-4} for the specific dispersion, k and V_0 were calculated for the normal paraffins and for the average data representing each group of paraffin isomers. This method of calculation, in which a constant specific dispersion is assumed, is definitely superior to our previous calculations in which the observed experimental dispersion was used for each compound. The average number of dispersion electrons per formula bond (k) obtained in this way is constant and independent of molecular weight as shown in Fig. 1. The data for the normal paraffins up to about 170 molecular weight are precise and form a good line. In the case of the average paraffins a good line is also obtained, and hydrogenated rubber would fall on an extrapolation of this line.

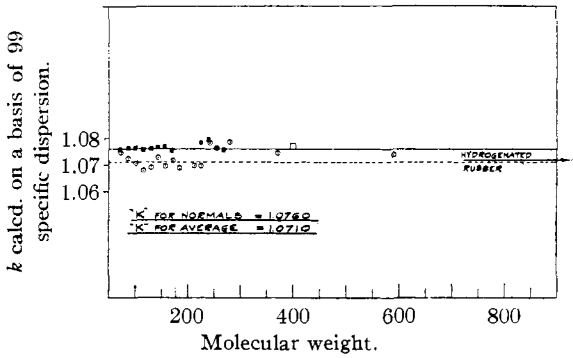

Fig. 1.—Normal paraffins, ■; average paraffins, ⊙; Kreulen's paraffins, ⊡.

Based on these calculations, the average value for the number of dispersion electrons per bond in normal paraffins may be taken as 1.0760 ± 0.0005. In our previous publication,[4] a slightly lower value of k, namely, 1.066, was recommended for both normal and average paraffins. It is rather difficult to establish the value of this constant with precision, since the mathematical function by which it is determined is very sensitive to a small difference in dispersion data. Graphically, one may think of k and V_0 as being determined by the intersection of the curves relating k to V_0 for the Sellmeier equation, when k and V_0 are calculated for various spectral lines such as H_α and H_β. The slopes of these lines are almost identical, so that the point of intersection shifts considerably with small changes in the position of either line. At the present time, we feel that it is a justifiable simplification to assume that k is a constant, 1.0760 ± 0.0005 in the normal paraffin homologous series. In the case of the "average" paraffin homologous series, the calculated average value for the number of dispersion electrons per bond is 1.0710 ± 0.005.

Taking k for the normals = 1.0760 and k for the average paraffins = 1.0710 as constants, the values of V_0 were recalculated. When these values for the characteristic frequency of the dispersion electrons are plotted against density, an excellent straight line is obtained for the normal paraffins; and a good straight line is obtained for the average paraffins as shown in Fig. 2.

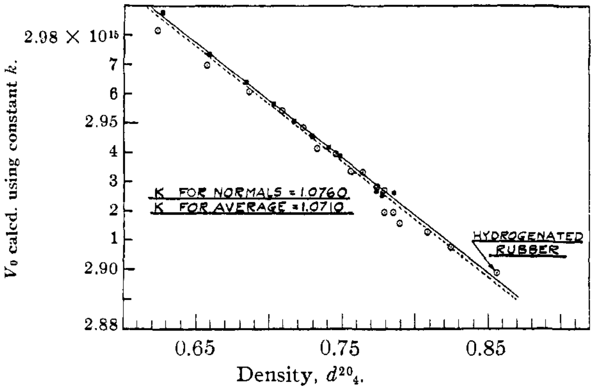

Fig. 2.—Normal paraffins, ■; average paraffins, ⊙. Equations: normals, $V_0 = (3.2313 - 0.3911d)\ 10^{15}$; average, $V_0 = (3.2301 - 0.3911d)\ 10^{15}$.

This applies to the relation between frequency and density where density is changed by changing molecular weight. The equations corresponding to these lines are

$$\text{Normal paraffins, } V_0 = (3.2313 - 0.3911d)10^{15} \quad (5)$$

$$\text{Average paraffins, } V_0 = (3.2301 - 0.3911d)10^{15} \quad (6)$$

Substituting in Equation 3 the values of ϕ from Equation 4 and of V_0 from Equation 5 or Equation 6, we obtain Equation 7 for the refractive index of paraffins at any temperature or pressure and for any wave lengths of light. It is, of course, necessary to know the density at 20° and 1 atmosphere pressure and under the conditions for which the refractive index is wanted.

$$n^2 - 1 = \frac{d_{t,p}kb\ 4.8861 \times 10^{31}}{M\{[(F - 0.3911d^{20}{}_4) + 0.47\ (d^{20}{}_4 - d_{t,p})]^2 \times 10^{30} - V^2\}} \quad (7)$$

Using Equation 7, it is possible to calculate refractive indices and see what degree of agreement is obtained with experimental data.

The average deviation of the normal paraffin refractive indices as calculated by this method is 0.0002, and there is no evidence of trend of deviation with molecular weight. The agreement by our method of calculation is free from systematic trend and is about four times as accurate as is obtained using the Eisenlohr constants[8] and the Lorentz–Lorenz equation.[16–18] Equation 7 is, furthermore, accurate for any wave length of light in the visible spectrum.

The agreement in the case of the averages is not quite so good. In this case there are few deviations worse than 1 in the third decimal place. The average deviation is 5 in the fourth decimal of the refractive index, but the deviation of the average (considering sign) is only 1 in the fourth decimal. Again there is no definite evidence of trend with molecular weight. The agreement, although not perfect, is better than is obtained if the Eisenlohr atomic refraction constants are used.

In calculating the refractive index of individual paraffin isomers, one may use the k and V_0 for the average paraffin of the same molecular weight and the actual density of the isomer in question. The refractive indices calculated in this way, without any structural constants, agree almost as accurately with experimental values as those calculated by the correlative system of Huggins[19] which involves the use of several structural constants.

Effect of Temperature and Pressure.—Equation 3 and the corresponding dielectric constant equation have been shown by Kurtz and Ward[4,6] to be suitable for representing the effect of temperature or pressure on either the density–refractive index or density–dielectric constant relation for hydrocarbons. In deriving this equation, the empirical but exact Eykman equation[20–23] was used as a guide in regard to the proper relation to expect between the above constants. In Table XVII of ref. 4, it was shown that for five saturated compounds the slope $\psi = \Delta V_0/\Delta d$, is 0.47×10^{15}, the maximum value being 0.485×10^{15} and the minimum 0.455×10^{15}. The recommendation was made that 0.47×10^{15} be used for ψ in calculating all data for paraffins and naphthenes. The question naturally arises that there may be a mathematical incompatibility

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[16] H. A. Lorentz, *Ann. Physik*, **9**, 641 (1880).

[17] H. A. Lorentz, "Theory of Electrons," B. G. Teubner, Leipzig, 1909, p. 141.

[18] H. Lorenz, *Ann. Physik*, **11**, 70 (1880).

[19] M. L. Huggins, THIS JOURNAL, **63**, 116 (1941).

[20] J. F. Eykman, *Rec. trav. chim.*, **14**, 185 (1895).

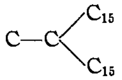
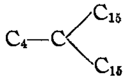
[21] J. F. Eykman, "Recherches Refractometriques, Naturkundige Verhandlingen Hollandsche Maatschappij Wetenschappen." Edited by A. F. Holleman, printed in French by Erven Loosjes, Harlem, 1919.

[22] W. Nernst, "Theoretical Chemistry," The Macmillan Co., London, 1911, p. 314.

[23] R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **60**, 511 (1938).

TABLE I

COMPARISON OF EQUATION 7 AND THE LORENTZ–LORENZ EQUATION FOR CALCULATING REFRACTIVE INDICES AT ELEVATED TEMPERATURES

Compound	Ref.	Temp., °C.	Density	Refractive index Exp.	Difference from experimental refractive index	
					Equation 7	Eisenlohr and Lorentz–Lorenz
Normal C_{20}	20, 21	38.3	0.7762	1.4355	−0.0005	−0.0027
		136	.7110	1.3966	− .0003	− .0049
Normal C_{32}	24	84	.8687	1.4313	− .0001	− .0036
Branched C_{32}	25	40.5	.8096[a]	1.4517	− .0002	− .0006
		71.5	.7905[a]	1.4395	+ .0006	− .0006
Branched C_{35}	25	19	.8244[a]	1.4602	− .0001	.0000
		70	.7913	1.4408	− .0005	− .0019

[a] Corrected to indicated temperature from the nearest temperature at which experimental data were available for liquid density; all densities are for liquid state.

between the statement that ψ is a constant for all temperature and pressure ranges and that the Eykman function is also constant. This was investigated by assuming that the Eykman function was absolutely precise and calculating the value of ψ corresponding to three density increments.

This was done by calculating the Eykman constant based on $n^{20}D$ and $d^{20}{}_4$ for normal C_5, C_{12}, and C_{19}, and then calculating the refractive index corresponding to the indicated densities with the aid of the Eykman equation and a table of constants calculated for the equation.[26] These refractive indices are then substituted in Equation 8.

$$V_0 = \sqrt{\frac{B}{n^2 - 1} + V^2} \qquad (8)$$

The term B is calculated using Equation 2.

For normal pentanes the slope for the first density increment (0.6262 to 0.7030) is 0.49 × 10^{15} and for the last density increment (0.7798 to 0.8565) is 0.46 × 10^{15}. For normal C_{19} the corresponding slopes are 0.48 × 10^{15} and 0.45 × 10^{15}. It is clear that if the basic assumptions underlying this calculation are correct there is a slight change in slope ψ depending on the density range considered, but that 0.47 × 10^{15} is a good average value.

In using Equation 3 to calculate refractive indices at high temperatures, a variation of ±0.02 × 10^{15} in the slope ψ causes only small difference in the calculated refractive index. For example, the refractive indices of eicosane have been calculated using Equation 3 for 38.3 and 136°, temperatures at which Eykman gives experimental data. In making these calculations, the density for the hypothetical liquid state at 20° was calculated using a relation between coefficient of expansion and molecular weight recently developed.[27] At 136° there is a difference of 0.0007 between the refractive indices calculated using $\psi = 0.45 \times 10^{15}$ and 0.49×10^{15}. The refractive index based on $\psi = 0.47 \times 10^{15}$ is 0.0003 lower than the experimental value. Considering the wide range of temperature over which these calculations were made, we believe that the agreement is quite good, and, furthermore, that these calculations justify the use of the average value 0.47 × 10^{15} for the slope ψ. Similar calculations for the alpha and beta lines of hydrogen using $\psi = 0.47 \times 10^{15}$ show equally good agreement with Eykman's data.

Table I gives a comparison of experimental refractive indices with refractive indices calculated using Equation 7 and with refractive indices calculated using the Eisenlohr values for carbon and hydrogen and the Lorentz–Lorenz equation.

Refractive indices calculated with Equation 7 are usually correct within 0.0005 whereas the values calculated with the Eisenlohr constants and the Lorentz–Lorenz equation in three out of four cases are in error by 0.0020 or more.

The data of Eykman for normal eicosane are especially worthy of attention both because of the

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(24) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1939.

(25) H. Suida and R. Planckh, *Ber.*, **66**, 1445 (1935).

(26) A limited number of photostatic copies of this table are available for distribution by the authors.

(27) M. R. Lipkin and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **13**, 291 (1941).

precision of his experimental work and the range of temperature covered.

For the temperature interval 38.3 to 136°, his experimental data show a change in refractive index of 0.0389 unit, whereas Equation 7 predicts a change of 0.0387 unit and the Lorentz–Lorenz equation predicts a change 0.0414 unit. The refractive index of eicosane changes about 0.0100 unit for every 25°, and the Lorentz–Lorenz equation predicts a change of 0.0107 unit for this temperature and density increment. Since with precise equipment, refractive indices can now be measured within about 0.00005 unit, the indicated discrepancy of 0.00070 per 25° is much greater than any reasonable experimental error in precise work.

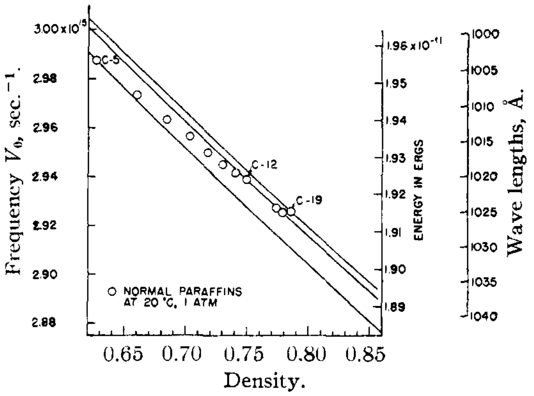

Fig. 3.

In Fig. 3, frequency has been plotted against density for normal paraffins from C_5 to C_{19} to show the effect of temperature or pressure on the frequency–density relationship. It is clear from this graph that if all the lower members of the homologous series were compressed to the density of C_{19}, the frequencies at this density would increase from C_5 to C_{19} as the molecular weights increase.

Considering these frequencies from a quantum point of view, $V_0 \times h = E$. The right-hand coordinates in the graph give the energy in ergs × 10^{-11} corresponding to these frequencies and also the corresponding wave lengths in ångström units. This energy is equal to the average difference in energy between the lower energy state E_1 and the higher energy state E_2 between which the valence electrons can shift.

The bond energies here discussed should, of course, not be confused with bond energies calculated from thermal data.[28]

The frequencies and energies calculated from dispersion data probably represent average values. Ethane[29] absorbs at about 1600 Å. and lower, but we are not aware of any absorption studies which report data for paraffins in the range in which we are especially interested, namely, 1000 to 1040 Å.[30]

At the present time, we do not feel that it is profitable to indulge in speculation concerning possible mechanisms by which the average frequency, and hence average energy difference between the possible states of the valence electrons, becomes a function of the density in hydrocarbons.

We hope that our calculations will encourage research workers to obtain more precise experimental data in this field so that a thoroughly sound experimental foundation will be available for future theoretical developments.

Additional precise data are needed on the isomer effect, and on the effect of temperature and pressure on the relation between density and either refractive index or the dielectric constant of non-polar liquids. It would also be very interesting from a theoretical point of view if good absorption data could be obtained in the range of 500 to 2000 Å.

We hope to apply this type of calculation to saturated cyclic compounds.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Donald Hornig and Mr. I. W. Mills in carrying out a part of these calculations.

Summary

1. The modified Sellmeier–Drude equation

$$n^2 - 1 = \frac{B}{(V_0 + \phi)^2 - V^2}$$

is used to correlate refractive index–density data for both normal and average paraffins.

2. It is shown that there is approximately one dispersion electron per formula bond, and that the frequency is linear with the density in any homologous series.

3. It is shown that the refractive index of normal paraffins can be calculated within ±0.0002 and the refractive index of average paraffins within ±0.0005. Refractive index of paraffins can be calculated for any wave length of light, and for any temperature or pressure, provided the corresponding density is known.

4. The significance of the ϕ coefficient is

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[28] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 53.

[29] G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

[30] J. C. Boyce, *Rev. of Modern Phys.*, **13**, 1–33 (1941).

briefly discussed. The relationships between frequency V_0, energy in ergs, and wave length in ångström units corresponding to bonds in the normal paraffin homologous series are shown graphically. For any one paraffin, the shift in frequency and wave length caused by change in density is appreciable. Measurements of ultraviolet absorption of normal paraffins in the vicinity of 1000 Å. would be of great interest.

MARCUS HOOK, PENNA. RECEIVED FEBRUARY 17, 1941

[CONTRIBUTION FROM ALLERGEN INVESTIGATIONS, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, U. S. DEPARTMENT OF AGRICULTURE, AND THE ALLERGY CLINIC OF PROVIDENCE HOSPITAL, WASHINGTON, D. C.]

The Chemistry of Allergens. IV. An Electrophoretic Fractionation of the Protein–Polysaccharide Fraction, CS-1A, from Cottonseed[1]

BY JOSEPH R. SPIES, HARRY S. BERNTON AND HENRY STEVENS

Isolation and properties of an allergenic protein–polysaccharide fraction, CS-1A, from cottonseed have been described.[2] This fraction is of interest because the components separated from it possessed an unusual combination of chemical stability and immunological potency and specificity. Moreover, active components have been obtained in quantity sufficient for investigation of their chemical composition.

Although the electrophoretic method of Tiselius and others is now widely employed in protein chemistry, the use of direct current at high voltage for fractionating unbuffered protein solutions in preparative work has not been exploited as much as may be warranted. The earliest extensive application of high voltage electrophoresis for fractionating biologically active substances was that of Williams and co-workers.[3] The theory of this type of electrophoresis has been discussed adequately by Williams and Truesdail.[3a] Du Vigneaud and Irving, *et al.*, have recently used this method in fractionating the posterior pituitary hormones.[4]

The present paper describes a large scale electrophoretic fractionation of CS-1A and properties of the separated components. The four cathodic fractions, CS-51R, CS-52R, CS-53R and CS-54R[5] were isolated by picric acid precipitation and were further purified by recovery and reprecipitations. These fractions were characterized by potent allergenic activity, high nitrogen content and by the absence of significant amounts of carbohydrate. The anodic fraction CS-56 contained 48% polysaccharidic carbohydrate, and was lower in nitrogen content and allergenic activity than the cathodic fractions. Fraction CS-55, recovered from the cell which originally contained unfractionated CS-1A, corresponded in composition to fraction CS-56. A denatured solid, CS-57, precipitated during electrophoresis in cells 1+ and 2+, Fig. 1. Of all the fractions separated, CS-57 was lowest in nitrogen content, exhibited the least allergenic activity and was not studied further.

Evidence of chemical differences in composition of the fractions was obtained by determination of total and protein nitrogen, carbohydrate, sulfur and cystine content. Table I contains a summary of these data on the fractions obtained from 400 g. of CS-1A, and on sub-fractions obtained from them by chemical procedures.

Heidelberger and Avery[6] working with pneumococci first showed that polysaccharides contribute importantly to the specificity of these organisms. Subsequent investigations have revealed that polysaccharides are no less significant than proteins in contributing to the immunological specificity of many bacteria.[7] The polysaccharides of pneumococci were resistant to treatment with acid at room temperature. However, warming with acid produced reducing sugars with accompanying loss in specific activity.[8] Later, Heidel-

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[1] For Paper III of this series see Spies, Bernton and Stevens, THIS JOURNAL, **62**, 2793 (1940).

[2] (a) Spies, Bernton and Stevens, *J. Allergy*, **10**, 113 (1939); (b) Spies, Coulson, Bernton and Stevens, THIS JOURNAL, **62**, 1420 (1940).

[3] (a) Williams and Truesdail, *ibid.*, **53**, 4171 (1931); (b) Williams, Lyman, Goodyear, Truesdail and Holaday, *ibid.*, **55**, 2912 (1933); (c) Williams and Moser, *ibid.*, **56**, 169 (1934); (d) Williams, *J. Biol. Chem.*, **110**, 589 (1935).

[4] (a) Du Vigneaud, Irving, Dyer and Sealock, *ibid.*, **123**, 45 (1938); (b) Irving and du Vigneaud, *ibid.*, **123**, 485 (1938); (c) Irving, Dyer and du Vigneaud, THIS JOURNAL, **63**, 503 (1941).

[5] These four fractions are essentially equivalent to the protein fraction CS-13A previously described in Paper II of this series, 2b.

[6] Heidelberger and Avery, *J. Exptl. Med.*, **38**, 73 (1923).

[7] Landsteiner, "The Specificity of Serological Reactions," Charles C. Thomas, Baltimore, Md., 1936, reviews the subject of carbohydrates with respect to serological specificity.

[8] Heidelberger and Avery, *J. Exptl. Med.*, **40**, 301 (1924). Heidelberger, Goebel and Avery, *ibid.*, **42**, 727 (1925).