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Introduction. In Part 1 (Lab Note 64-16) the refractive index data for liquid normal hydrogen by Johns and Wilhelm [1937] were examined and, because of their relatively low precision, it was suggested that better values of refractive indices could be obtained by computation, starting with other data of higher accuracy. In outline, the proposed calculation involved the following steps: (1) From the published P-ρ-T correlation of this laboratory [Goodwin et al, 1963] to find the density of the desired state. (2) From J. W. Stewart's formula (Eq. 2 of Part 1) to calculate the specific dielectric polarization. (3) To equate this to the specific refraction at infinite wavelength by Maxwell's identity. (Recent accurate measurements of the dielectric constants of several gases by Dunn [1964] confirm this identity for substances like hydrogen which do not show anomalous dispersion.) (4) To calculate the specific refraction at the desired wavelength by a Cauchy-type dispersion formula (Eq. 1 of Part 1), the coefficients of which are determined from accurate published data for the dispersion of the gas at STP. Then to extract the refractive index value from the Lorentz-Lorenz (L-L) formula,

$$r = \frac{n^2 - 1}{\rho(n^2 + 2)}$$

In this part recent data by Belonogov and Gorbunkov [1963] will be analyzed, the data of Johns and Wilhelm will be examined more closely, and some much older data by Augustin [1915] and Scheel [1907] will be taken into account. Part 1 should be consulted for earlier references and notation.

Data of Belonogov and Gorbunkov. These authors have determined the refractive index of saturated liquid parahydrogen from about the n. b. p. (normal boiling point) to 30.5°K and at the wavelengths, 4360, 5460, and 5790 Å. They have also determined the refractive index of saturated liquid normal hydrogen at 5460 Å and over the same temperature range. Thus their temperature range meets that of Johns and Wilhelm at about the n. b. p. but does not overlap it. They are the only authors to have measured parahydrogen or the para-normal difference. The following comments may be made about their work.

- (1) Their claimed accuracy is ± 2 x 10⁻⁴ in the absolute values of n and ± 1 x 10⁻⁴ in

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the difference of refractive index between normal and parahydrogen. An image displacement method of measurement was used.

(2) Their data are presented in small graphs. I estimate the error in reading values of n from these graphs by an expandable scale and magnifier to be about $\pm 2 \times 10^{-4}$. This must be combined with their estimated experimental error of the same magnitude to give an overall error (rms) of the recovered data of about $\pm 3 \times 10^{-4}$. This corresponds to about $\pm 0.3\%$ in r . They present the data for both forms of hydrogen at 5460 \AA in one graph as a function of temperature and in another graph as a function of density. (The densities were obtained from the data of Goodwin et al. [1961].) It should be possible to estimate the graph-reading error by comparing the results read from these two graphs. On comparing specific refractions calculated from the data of the two graphs a consistent difference of about 0.3% was found. This corresponds to 3×10^{-4} in n . There was little overlap of the two sets. Thus it appears that the estimate above of reading error is conservative, but that detectable systematic inconsistencies exist between the different representations of the same data in the paper of Belonogov and Gorbunkov.

(3) The authors state that their results "correspond to the L-L formula with an accuracy of 5×10^{-5} ." The interpretation of this statement is obscure. The most conservative interpretation would seem to be that r is constant within limits equivalent to $\pm 5 \times 10^{-5}$ in n . However, the authors' claimed accuracy in n was only $\pm 2 \times 10^{-4}$. Also in order to obtain such a finding, the density would have to be known more accurately than 1 part in 2000. The density is not known this accurately. Thus it seems that the authors could not possibly have known either n or ρ accurately enough to support the statement quoted above. Nevertheless, the L-L relation seems to be obeyed, inasmuch as I find no consistent dependence of their values of r on ρ . However, in considering values of r for a particular form of hydrogen at a particular wavelength, variations from the mean as large as 0.5% were found indicating that the error estimate in (2) above is not conservative enough.

(4) Because of the apparent applicability of the L-L formula, all of the results at a given wavelength for a given form of hydrogen can be lumped together in an average value of r_λ , independently of the temperatures and pressures at which the individual

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measurements of n were made. The dispersion then can be expressed simply as the dependence of r_λ on λ . The average values of r_λ for parahydrogen at the three wavelengths are shown in figure 1 and table 1.

If these data are fitted by the Cauchy formula (Eq. 1 of Part 1), further evidence of imprecision is found, namely that the coefficient B is negative. This is readily seen if r_λ is plotted versus $1/\lambda^2$ as in figure 2, i. e. a simple curve through the three points of B & G is concave downwards. However, for the behavior to be physically realistic, both of the coefficients, A and B , must be positive, giving a dispersion curve of the shape shown schematically by the solid curve in the inset in figure 1. This behavior, corresponding to the equation preceding Eq. 1 of Part 1, consists of an asymptotic approach to a limiting value, r_∞ , at zero frequency and a rise to infinity at a frequency, c/λ_0 , corresponding to the ionization energy of the molecule. The negative B coefficient does not have much effect on the extrapolation to $\lambda = \infty$ but results in negative values near λ_0 (dotted curve in inset of figure 1); this is the physically unreal behavior just referred to. Obviously then, the dispersion formula must be truncated at the term in $1/\lambda^2$. The values of r_∞ and A in table 1 were obtained by least-squares fitting of the truncated formula to the three values of r_λ .

Data of Johns and Wilhelm. These data were considered in Part 1. Three refinements will now be introduced.

(1) The values of r_λ given in Part 1 were calculated from data at the n. b. p. only. However Johns and Wilhelm made measurements from the triple point to the n. b. p. The specific refractions showed no dependence on temperature or pressure. Hence average values of r_λ based on all of these data will be statistically more reliable than the n. b. p. values alone.

(2) The values of r in Part 1 were calculated using the densities of Onnes and Crommelin [1913] tabulated in Johns and Wilhelm's paper. It would be better to use modern density data. The correlation for normal hydrogen by Goodwin et al. [1961] has been adopted for this purpose. The latter densities are from 0.1 to 0.2% higher than the older values. Their use does not alter the conclusion that Johns and Wilhelm's specific refractions are independent of temperature and pressure. The net effect is to lower the average values of r_λ by 0.16 to 0.18%.

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(3) The temperature scale used by Johns and Wilhelm should be corrected to a modern basis. The only clue to what their scale was is their statement that the n. b. p. was 20.41°K . There was a PTR scale [Henning and Heuse, 1924] on which the n. b. p. of hydrogen had this value. If this were the one used, it would be reasonable to correct all of Johns and Wilhelm's temperatures by the factor $20.38/20.41$. I have rather arbitrarily chosen to do this. Another possibility is that Johns and Wilhelm were using a Leiden scale, but incorrectly. This could have come about by adopting the n. b. p. of -252.754°C reported by Keesom, Bijl, and Van der Horst [1931] combined with the assumption, $0^{\circ}\text{C} = 273.16^{\circ}\text{K}$. This would have been erroneous because Keesom et al. had based their n. b. p. on $0^{\circ}\text{C} = 273.13^{\circ}\text{K}$. If this were the source of Johns and Wilhelm's scale, then a translational shift by -0.03 deg would be in order. I have not found any other ways of accounting for their assumed value for the n. b. p. Either way of correcting their scale changes the specific refraction by only a few parts in 10^4 . The difference between the two ways just outlined is at most 1 part in 10^4 in r . This is insignificant, inasmuch as their claimed accuracy of 0.0003 in n corresponds to about ± 24 parts in 10^4 in r .

The new results after making the above three refinements are given in figures 1 and 2 and table 1. (They supersede the data given in Part 1.) The three points in figure 2 show downward curvature, the same defect noted in the data of Belonogov and Gorbunkov. Hence, the dispersion formula is again truncated after the term in $1/\lambda^2$.

Data of Augustin. These were determined at five wavelengths for saturated liquid at 745.52 mm. pressure. Using modern vapor pressure data, the temperature is found to be 20.316°K . The determination was made by measuring critical angles. The experiment was very similar to that of Johns and Wilhelm. However, because of the way in which the optical cell was constructed, the measurements gave the ratio of the refractive indices of saturated liquid and vapor, whereas the liquid refractive indices by Johns and Wilhelm were referenced to vacuum. Augustin obtained the refractive indices of the liquid from the above ratios by using estimated values of the refractive index of the vapor. He obtained these by assuming the L-L ratio to hold between STP and the 20.3° saturated vapor and by assuming the vapor to be ideal.

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The saturated vapor density that he calculated can now be seen to be 6% low. Although experimental refractive indices of the saturated vapor are still unavailable, this part of Augustin's procedure can now be improved upon by using ^{certain} modern data. In addition we can calculate n_λ at all five wavelengths, whereas Augustin had to omit one wavelength for lack of subsidiary data. Two procedures can be suggested:

- (a) Starting with experimental data for n_λ of the gas at STP, such as those described in Part 1, calculate r_λ from the L-L formula at the wavelengths used by Augustin. Assume that these values are valid for the saturated vapor at 20.3°K. Using modern data for the density of the saturated vapor, convert the r_λ values to n_λ for the saturated vapor by the L-L formula.
- (b) Start with the value of specific polarization at the density of the saturated vapor calculated from Stewart's formula (Eq. 2 of Part 1). Equate this to r_∞ . Use the accurate formula for dispersion of the gas at STP (Eq. 1 of Part 1) to convert this to values of r_λ at the desired wavelengths. The final step is the same as above.

Procedure (a) requires the L-L ratio to be constant over a very wide range of temperatures. Procedure (b) only requires the relatively minor dispersion corrections to be constant over this same range. Hence, (b) is to be preferred and so was used.

The density of the saturated vapor was found from the recent correlation by Stewart and Roder [1964]. The specific polarization at this density was calculated to be 1.00439 cm³/g. The values of n_λ for the vapor and, hence, those calculated for the liquid, are as much as 0.02% higher than Augustin's. The corrected values of r_λ are given in figures 1 and 2 and table 1.

In studying Augustin's paper one is impressed that his was a careful and precise work. This impression is supported by the appearance of figures 1 and 2, including the fact that the curvature in figure 2 is of the proper sign. Hence the three-term dispersion formula could be used to fit the data. Another evidence of the quality of this work is the fact that the saturated liquid density as determined by Augustin in a separate experiment is within 0.06% of modern data [Goodwin et al., 1961].

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Data of Scheel. The refractive index of the gas at 1 atm. and at two temperatures in the liquid air range as well as at STP was determined. The low temperature data, if they were accurate enough, would be of interest as midpoints in tracing the slight temperature variation of the L-L ratio from room temperature to the 20°K region. Unfortunately the data of Scheel for the gas at STP are substantially lower than the data from the five sources reviewed in Part 1. The difference approaches 1% in $(n_{760}^{\circ} - 1)$. Because of this evidence of systematic error, the low temperature data of Scheel were not analyzed.

Discussion. Figures 1 and 2 and table 1 compare four sets of specific refractions for normal hydrogen with one set for parahydrogen. Of the data for the liquid, those by Augustin are thought to be the most accurate, those by Belonogov and Gorbunkov the least accurate, and those by Johns and Wilhelm intermediate but not much more accurate than those of Belonogov and Gorbunkov. The data for the STP gas from K-K [Kohn, 1912; Kirn, 1921] and the values calculated for the liquid by the method of Lab Note 64-16 are based on much more accurate data of other kinds; however, it is a moot question how well either simulates the specific refraction of the liquid.

The comparison between normal and parahydrogen at 5460Å by Belonogov and Gorbunkov, if applicable at all wavelengths, would permit one to adjust all of the data to the same basis of o-p composition. The points of Johns and Wilhelm and of Augustin in figure 1, and these plus the K-K curve in figure 2 would be lowered relative to the others by the length of the arrow in each figure. Unfortunately, such an adjustment would worsen the overall agreement. This result, taken with the various deficiencies of the work of Belonogov and Gorbunkov that have been pointed out, suggest that their value for the normal-para difference should not be accepted in the absence of confirmation. It is unfortunate that Stewart did not determine this difference in his recent measurements of dielectric constant.

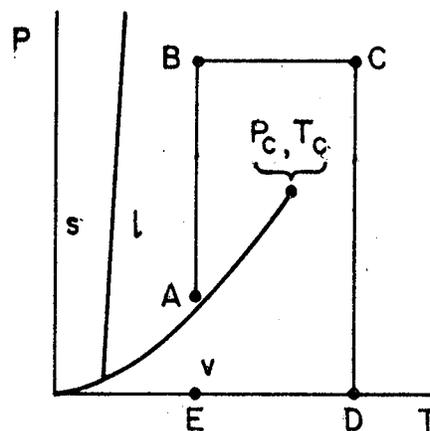
Because of the discordance among the experimental measurements on the liquid, it is still suggested that the method of estimation given in Part 1 should be used in preference to the experimental data. Table 2 gives a summary of how well the refractive indices calculated in that way agree with the experimental values. It will be seen that the agreement is comparable to the agreement of the experimental

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investigations among themselves. This comparison was made without applying any corrections for the para-normal difference. If the difference found by Belonogov and Gorbunkov could be assumed to apply under all conditions, the deviations listed in table 2 for Johns and Wilhelm and for Augustin would all be increased by 6 units.

It is sometimes suggested that it is more accurate to derive dielectric constants from refractive indices by the Maxwell relation, $\epsilon = n_{\infty}^2$, than to determine them directly. This is undoubtedly true for gas at moderate pressures, because the refractive index can be determined by very sensitive interferometric methods. However, the opposite is likely to be true for liquids, as this study exemplifies, because of the necessity of using less accurate deviation methods for the refractive index. Interferometers have apparently not been used for absolute measurements on liquids because of the impossibility of counting the passage of fringes continuously while isothermally attenuating the sample to a vacuum; i. e. the discontinuity at the liquid-vapor phase change destroys the continuity of the fringe count. Yet it is obvious that continuity could be maintained in principle by following a path in the P-T plane that would pass above the critical point and not intersect the coexistence line. Thus in the schematic diagram, to get from A to E without crossing the coexistence curve, one could follow the path ABCDE. Considerable care would have to be taken to maintain homogeneity of density in the optical cell during such a change; otherwise the fringe pattern would be lost. Either the Rayleigh or the Fabry-Perot refractometer would be suitable [Candler, 1951]. Sensitivity of the order of 1×10^{-6} in n with cell lengths as short as 1 cm would be feasible.



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Table 1
 Dispersion of hydrogen

λ	r_{λ} , cm ³ /g				
	B & G, liquid		J & W, liquid	Aug., liquid	K-K,* gas STP
A	para	normal	normal	normal	normal
4047				1.0556	
4358-60	1.056		1.050	1.0480	1.0508
5460-61	1.032	1.038	1.032	1.0319	1.0350
5790	1.026			1.0292	
6563				1.0246	
6939			1.018 ₅		
∞	0.988		0.998	1.0106	1.0083
10 ⁶ A	1.301		0.984	0.5165	0.7800
10 ¹² B				3.632	0.4951
Av. Dev.**	0.00037		0.00043	0.00009	

* See Part 1 for origins of this column.

** Average absolute deviation of r_{λ} as calculated by the dispersion formulas from the experimental values.

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Table 2

Summary of deviations, $10^4(n_{\text{calc.}} - n_{\text{exptl.}})$, of refractive indices of liquid hydrogen calculated by the formulas of Lab Note 64-16 from experimental values. Comparisons were made without regard to ortho-para composition.

λ A	Belonogov & Gorbunkov para-H ₂			Johns & Wilhelm normal-H ₂			Augustin normal-H ₂
	Av. Dev.	Max. Dev.	No. points	Av. Dev.	Max. Dev.	No. points	Dev. *
4047							-1.1
4358-60	-8.0	-15	7	-3.6	-7	8	-0.6
5460-61	+0.1	+5	7	-0.9	-7	9	-0.1
5790	+2.5	+8	7				-0.5
6563							-1.3
6939				+3.	+4	2	
Wtd. Av.	-1.8			-1.6			-0.7

* One experimental point at each wavelength

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Figure Captions

Figure 1. Specific refraction of liquid hydrogen as a function of wavelength.

The two curves show the extremes given by the formulas of Lab Note 64-16 for saturated liquid. The lower one is for the triple point density. The upper one is for the density at which p and r are maximum. This density is near critical. (Actually it is the same as the density of saturated liquid at 32.7°K.) With further decrease of density, p and r decrease again towards the lower curve. (See figure 4 of the paper by Stewart for the density variation of p .) The densities with which the curves are labelled are in units of g/cm^3 . For explanation of the inset, see the text.

Figure 2. Specific refraction of hydrogen plotted according to the Cauchy dispersion formula.

(K-K refers to the data by Koch and Kirn for the gas at STP described in Part 1. The symbol S shows the range of values of $p (= r_\infty)$ obtained by Stewart corresponding to the range of liquid densities indicated in figure 1.)

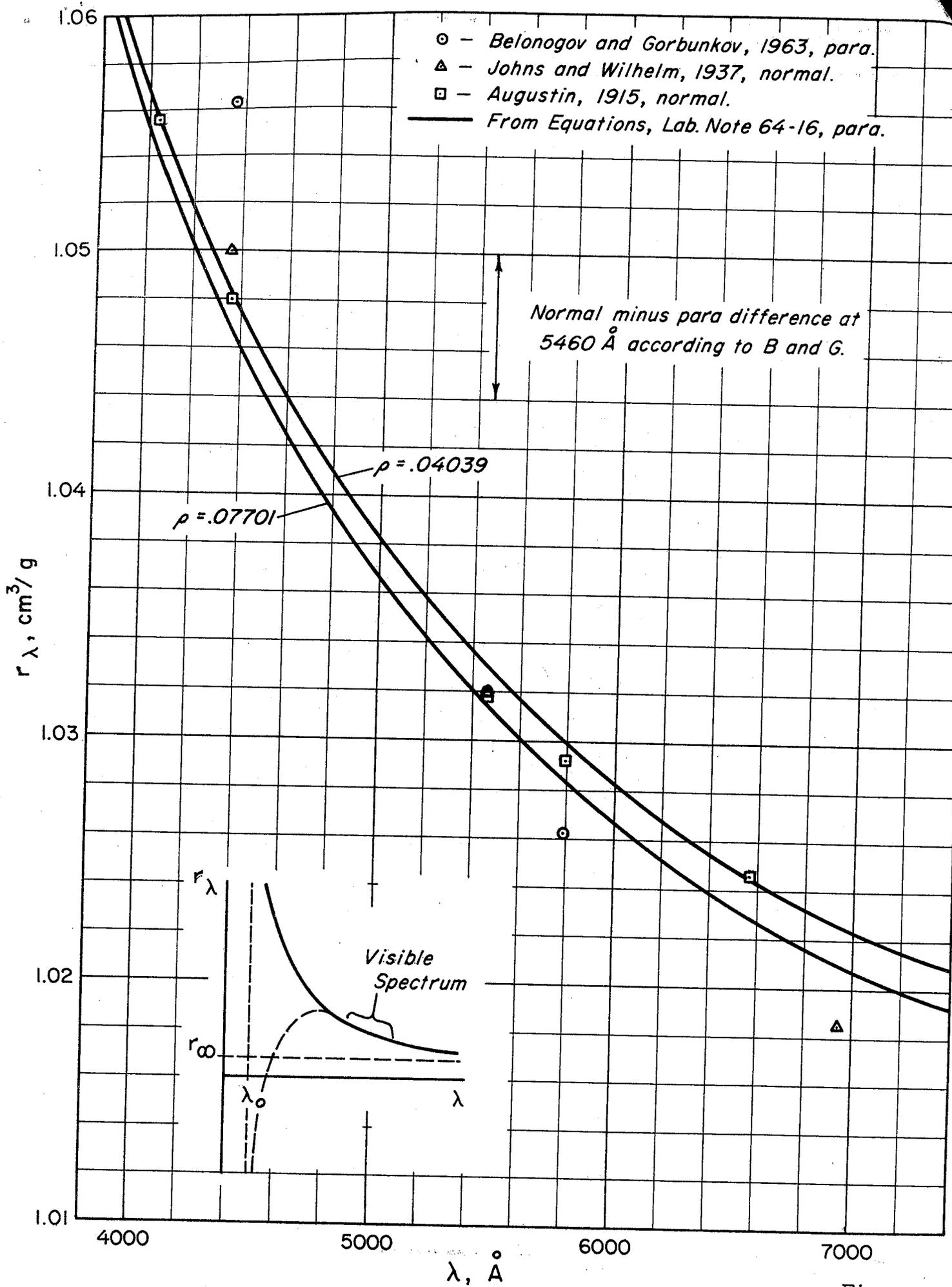


Figure 1

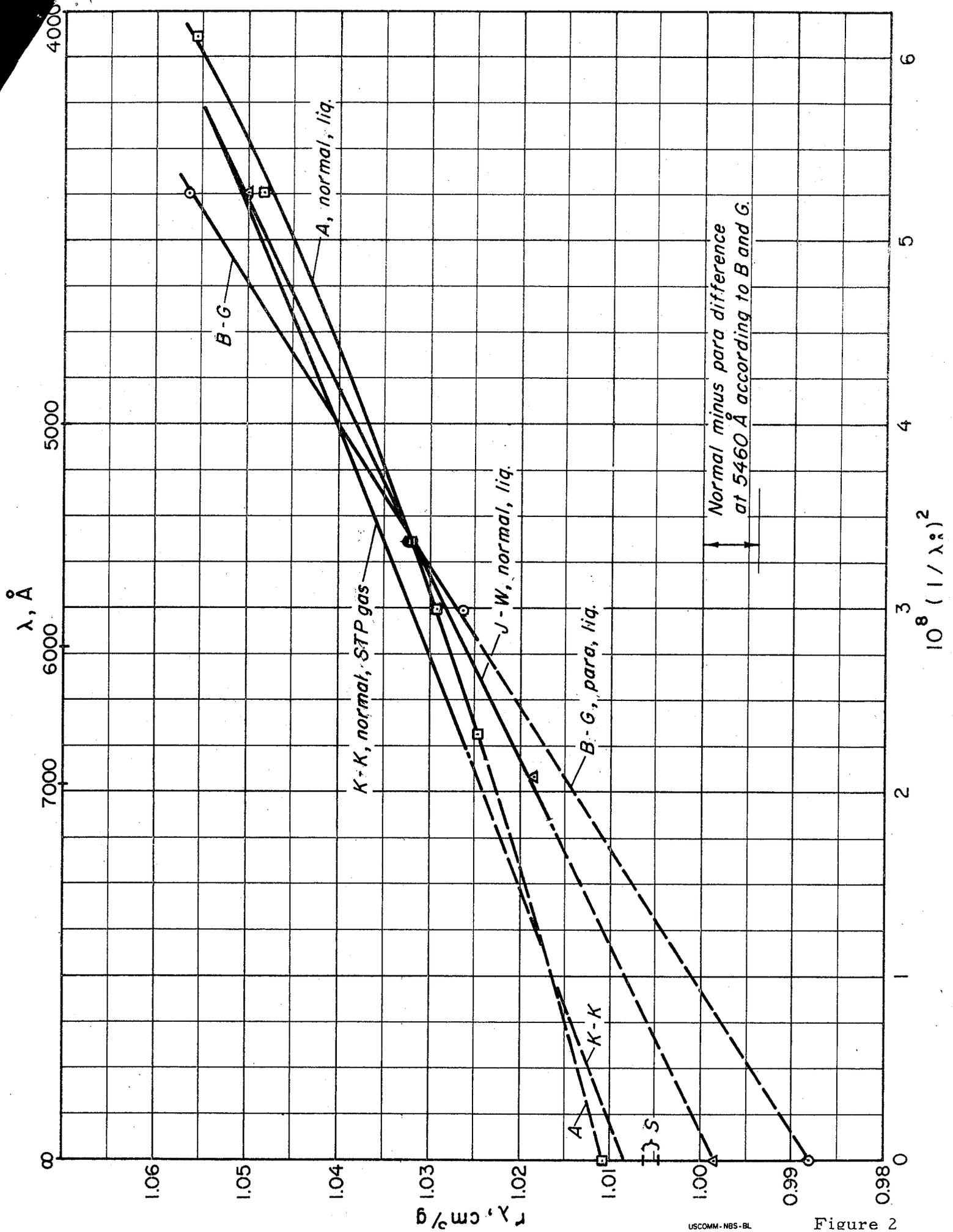


Figure 2