# Refractive Indices and Dielectric Constants of Liquids and Gases under Pressure

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(Received February 23, 1949)

Several interpolation formulas are given which reproduce refractive index and dielectric constant data for liquids and gases at high pressures. These formulas involve functions of the refractive indices and dielectric constants which appear in the formulas of Lorentz-Lorenz, Clausius-Mosotti, Gladstone and Dale, the empirical Eykman formula, etc. One formula shows the reciprocals of these functions to be linear in the specific volumes at various pressures. Another interpolation formula, involving the reciprocals of the same functions, contains a logarithmic term which is similar to that appearing in the Tait equation for compressibilities of liquids. The parameters involved in the Tait equations for compressibilities and in the analogous interpolation formula for refractive indices and dielectric constants are discussed.

The article also shows that the Tait equation which has been so successfully adapted to compressibility data of liquids can also be applied to gases.

## INTRODUCTION

IN a recent article[1] it was shown that the compressions[2] of alcohol, water and their mixtures calculated from the refraction formulas of Lorentz-Lorenz and of Gladstone and Dale are a linear function of the observed compressions of the solution. A logarithmic equation is given which reproduces with great precision the refractive indices of alcohol, water, and their mixtures under pressure; the logarithmic term is the same as that in the Tait equation for compressibilities, and the part of the equation containing the refractive indices involves the same functions of $n_P$ which appear in the formulas of Gladstone and Dale, Lorentz-Lorenz, etc.

It is the purpose of this paper to show that the results of the above article can be extended to existing data of both refractive indices and dielectric constants of liquids as well as to gases at high pressures.

Of the important formulas for the refractive index or dielectric constant of a substance which give a specific refractive or specific polarization "constant," all have the form $f(\nu_P)\nu_P = C$, where $f(\nu_P)$ is a function of the refractive index $n_P$ or the dielectric constant $\epsilon_P$, $\nu_P$ is the specific volume and $C$ the "constant." Where the formula is applied to solutions on which the pressure is varied, the expression

$$1 - [f(\nu_0)/f(\nu_P)] = k_P' \qquad (1)$$

would equal the observed compression, $k_P$, if $C$ remained constant. Characteristic functions are the Lorentz-Lorenz expression $(n^2-1)/(n^2+2)$, Gladstone and Dale's $(n-1)$, the Newton expression $(n^2-1)$ and the empirical function of Eykman $(n^2-1)/(n+.4)$. In all of these expressions $n_P{}^2$ may be replaced by $\epsilon_P$ to

obtained the corresponding formula involving dielectric constants.

It has generally been found that with none of these functions $f(\nu_P)$ can the observed compressions, $k_P$, of the solutions be computed from Eq. (1) with any great accuracy;[1,3,4] but Eq. (1) has frequently been used as a criterion in selecting the most suitable formula $f(\nu_P)\nu_P = C$ applicable to a particular substance. It will, however, be shown here that the compressions, $k_P'$, computed from Eq. (1), may be taken as a linear function of the observed compressions $k_P$. Accordingly, we may write

$$k_P' = m'k_P + b', \qquad (2)$$

where $m'$ and $b'$ are constants for a given substance. A more useful equation which is equivalent to (2) is obtained if we replace $k_P$ by $(v_0 - v_P)/v_0$ and $k_P'$ by the left member in Eq. (1). We obtain the expression

$$1/f(\nu_P) = m\nu_P + b, \qquad (3)$$

where $m$ and $b$ are constants independent of the pressure. Equation (3) will be shown to hold for existing data at high pressures both for the refractive indices and dielectric constants of liquids and gases. The forms of the function $f(\nu_P)$ in Eq. (3) may be those of theoretical significance already mentioned as well as others which have no theoretical foundations, such as for example, $f(\nu_P) = \nu_P$, etc. Though a number of these forms have been examined, only the Clausius-Mosotti and Lorentz-Lorenz functions, because of their theoretical interest, will be considered.

The equation, proposed by Tait for water,

$$dk_P/dp = C/(B + P),$$

has been shown in recent years,[1,5] notably by Gibson,

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[1] J. S. Rosen, J. Opt. Soc. Am. **37**, 932 (1947).

[2] The symbols used in this article are the following: $n_P$, $\epsilon_P$ and $v_P$ are the refractive index, dielectric constant and specific volume, respectively, at pressure $P$. The subscript 0 indicates atmospheric pressure ($P=0$). The bulk compression, $k_P$, is $-(v_P-v_0)/v_0$. Where the symbol $\nu_P$ occurs in the function $f(\nu_P)$ it will designate $\epsilon_P$ or $n_P{}^2$, and $f(\nu_P)$ will refer to the same function of $\epsilon_P$ or $n_P{}^2$.

[3] W. C. Röntgen and L. Zehnder, Ann. d. Physik **44**, 49 (1891); G. Quincke, *ibid.* **44**, 774 (1891).

[4] R. E. Gibson and J. F. Kincaid, J. Am. Chem. Soc. **60**, 511 (1938).

[5] Harned and Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1943), p. 270; P. W. Bridgman, Rev. Mod. Phys. **18**, 17 (1946); H. Carl, Zeits. f. physik. Chemie **101**, 238 (1922).

to represent successfully the compressibilities of liquids. This equation involves two parameters[6] $C$ and $B$ both independent of the pressure; $B$ is a function of the temperature, concentration (in mixtures),[1] and the properties of the solution; while $C$ is approximately independent of the temperature. It will be shown in this article that Tait's equation can also be applied to gases. In the integrated form this equation is

$$v_{P'} - v_P = v_0 C \ln\{(P+B)/(P'+B)\}, \qquad (4)$$

where the initial pressure, usually one atmosphere, is $P'$.

From Eq. (3), we have

$$\frac{1}{f(\nu_{P'})} - \frac{1}{f(\nu_P)} = m(v_{P'} - v_P).$$

If we substitute (4) into this equation, we obtain

$$\frac{1}{f(\nu_{P'})} - \frac{1}{f(\nu_P)} = A \log\left(\frac{P+B}{P'+B}\right) \qquad (5)$$

where $A$ and $B$ are constants for a given substance. If initially the pressure is the atmospheric pressure, and if the pressure range is large, it is most convenient to set $P'$ equal to zero. A better adjustment of the data may be obtained by replacing $(P'+B)$ by a third parameter, but in general this is not justified either by the accuracy of the data or the additional computation involved.

In this article we will justify Eqs. (3) and (5) as interpolation formulas for the considerable body of refractive index and dielectric constant measurements at high pressures for both liquids and gases. The Clausius-Mosotti and Lorentz-Lorenz functions will be adjusted by the method of least squares to these equations, but for Eq. (5) we will also study the form $f(\nu_P) = \nu_P$.

## THE INTERPOLATION FORMULAS

The literature on the subject of refractive indices and dielectric constants at high pressures contains some precedence for Eq. (3) and (5). Danforth,[7] in a much quoted paper on the dielectric constants at high pressure for some ten organic liquids, finds that the reciprocal of the Clausius-Mosotti expression $\rho_P/f(\epsilon_P)$ when plotted against the density $\rho_P$ gives a straight line for most liquids. This is evidently similar to Eq. (3), with $1/f(\epsilon_P) = (\epsilon_P+2)/(\epsilon_P-1)$. Owen and Brinkley,[8] on theoretical grounds, derive the Eq. (5) with $f(\nu_P) = \epsilon_P$ and $P' = 1$, and adapt the equation to data on dielectric constants at high pressure, and to the refractive indices of one non-polar liquid (benzene). Keyes and Kirk-

wood[9] find an expression similar to Eq. (3) to hold for their dielectric constant measurements on carbon dioxide and ammonia for various temperatures and pressures.

We shall have occasion later in this article to comment further on the work in these papers.

Older formulas on the refractive indices of binary mixtures at atmospheric pressure are reminiscent of the equations evolved above. The formulas of Pulfrich and Hubbard[10] resemble closely Eq. (1). Since, however, at atmospheric pressure the compressions of the mixture cannot enter, the right member of Eq. (1) is replaced by an analogous term which involves the ratio of the actual volume of the mixture and its volume calculated by a simple rule of mixtures. The interpretation of such a

TABLE I. The constants $m$ and $b$ of the equation $1/f_P = mv_P + b$, where $1/f_P = (\epsilon_P+2)/(\epsilon_P-1)$, evaluated by the method of least squares from dielectric constant data for liquids at high pressures. In the last two columns are shown the average and maximum percent difference between the observed and computed values of the dielectric constants. The pressures and volumes are in the units of the original data.

| Liquid | $t°C$ | $P_{max}$* | $m$ | $b$ | $(\%)_{av}$ | $(\%)_{max}$ |
|---|---|---|---|---|---|---|
| **Data of Danforth**** | | | | | | |
| Ethyl ether | 30 | 12000 | 1.17659 | 0.31125 | 1.21 | 2.74 |
| Ethyl ether | 75 | 12000 | 1.42582 | 0.06676 | 1.16 | 2.52 |
| Pentane | 30 | 12000 | 2.63595 | 0.36305 | 0.06 | 0.33 |
| Ethyl alcohol | 30 | 12000 | 0.12407 | 0.97643 | 0.38 | 1.08 |
| Ethyl alcohol | 0 | 12000 | 0.09448 | 0.99580 | 0.57 | 1.38 |
| Hexyl alcohol | 30 | 4000 | 0.23520 | 0.96426 | 0.59 | 0.83 |
| Hexyl alcohol | 75 | 8000 | 0.38421 | 0.90341 | 0.58 | 0.92 |
| Bromobenzene | 30 | 4000 | 1.01806 | 1.01761 | 0.15 | 0.35 |
| Bromobenzene | 75 | 8000 | 1.16001 | 0.94717 | 0.08 | 0.23 |
| Chlorobenzene | 30 | 4000 | 0.91212 | 0.77397 | 0.27 | 0.43 |
| Chlorobenzene | 75 | 8000 | 0.96532 | 0.76365 | 0.17 | 0.33 |
| Carbon bisulfide | 30 | 12000 | 3.03747 | 0.38371 | 0.48 | 1.03 |
| Carbon bisulfide | 75 | 12000 | 3.15413 | 0.31914 | 0.21 | 0.38 |
| Eugenol | 30 | 3000 | 0.48120 | 0.87206 | 0.39 | 0.79 |
| Glycerine | 30 | 12000 | 0.16428 | 0.94074 | 0.41 | 0.93 |
| Glycerine | 0 | 8000 | 0.13400 | 0.95619 | 0.20 | 0.38 |
| $i$-Butyl alcohol | 0 | 12000 | 0.12782 | 0.99198 | 0.42 | 0.86 |
| $i$-Butyl alcohol | 30 | 12000 | 0.17220 | 0.96906 | 0.36 | 0.67 |
| **Data of Chang**[a] | | | | | | |
| Carbon bisulfide | 75 | 12000 | 3.31543 | 0.19076 | 0.23 | 0.37 |
| Carbon bisulfide | 30 | 12000 | 3.27849 | 0.22453 | 0.41 | 1.77 |
| $i$-Amyl alcohol | 22.4 | 12000 | 0.26914 | 0.89999 | 1.85 | 2.19 |
| Ethyl ether | 30 | 12000 | 1.10326 | 0.35194 | 1.04 | 2.93 |
| Ethyl ether | 75 | 12000 | 1.34818 | 0.11343 | 0.62 | 2.93 |
| Toluene | 30 | 9500 | 2.43974 | 0.34378 | 0.13 | 0.31 |
| **Data of Kyropoulos**[b] | | | | | | |
| Carbon bisulfide | 20 | 3000 | 3.35849 | 0.16093 | 0.08 | 0.16 |
| Ethyl alcohol | 20 | 3000 | 0.10254 | 0.99178 | 0.25 | 0.37 |
| Methyl alcohol | 20 | 3000 | 0.08320 | 0.98660 | 0.14 | 0.21 |
| Water | 20 | 3000 | 0.04890 | 0.98860 | 0.08 | 0.31 |
| Acetone | 20 | 3000 | 0.14357 | 0.96469 | 0.27 | 0.48 |
| Ethyl ether | 20 | 3000 | 1.29268 | 0.08743 | 0.53 | 0.90 |

\* The pressures of Chang and Kyropoulos are in kg cm² those of Danforth's are in atmospheres.
\*\* See reference 7.
[a] Z. T. Chang, Chinese J. Phys. 1, (No. 2), 1 (1935).
[b] S. Kyropoulos, Zeits. f. Physik 40, 507 (1926).

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[6] When the true compressibility $dk/dP$ at atmospheric pressure is known only one parameter $B$ is necessary. This is especially important when adjusting data to the equation by the method of least squares. See reference 1.
[7] W. E. Danforth, Jr., Phys. Rev. 38, 1224 (1931).
[8] B. B. Owen and S. R. Brinkley, Jr., Phys. Rev. 64, 32 (1943).

[9] F. G. Keyes and J. G. Kirkwood, Phys. Rev. 36, 754 (1930); ibid. 36, 1570 (1930).
[10] International Critical Tables, Vol. VII, p. 65. The formulas for the indexes of refraction for binary mixtures are discussed here and a bibliography is given.

TABLE II. The constants $m$ and $b$ of the equation $1/f_P = mv_P + b$ evaluated by the method of least squares from dielectric constant data at high pressures for gases and from refractive indices for liquids and gases. The average and maximum percent deviations between the observed and calculated values of $\epsilon_P$ (or $n_P$) are given in the last columns. The pressures and volumes are in the units of the original data.

| Substance | $t°C$ | $P_{max}$ | $m$ | $b$ | $(\%)_{av}$ | $(\%)_{max}$ |
|---|---|---|---|---|---|---|
| **Dielectric Constants of Gases\*** | | | | | | |
| $1/f_P = (\epsilon+2)/(\epsilon-1)$ | | | | | | |
| Carbon dioxide (liquid) | 0 | 200[a] | 128.733 | −0.03195 | 0.06 | 0.12 |
| Carbon dioxide | 35 | 100 | 132.4435 | −0.7808 | 0.54 | 3.02 |
| Carbon dioxide | 100 | 151 | 133.7713 | −0.7962 | 0.04 | 0.24 |
| Ammonia | 100 | 55 | 23.9453 | −0.2956 | 0.03 | 0.10 |
| Ammonia | 175 | 100 | 27.5442 | −0.2266 | 0.06 | 0.15 |
| **Refractive Indices of Gases and Liquids** | | | | | | |
| $1/f_P = (n_P^2+2)/(n_P^2-1)$ | | | | | | |
| Carbon dioxide[b] | 32 | 122[e] | 3294.03 | 0.0363 | 0.13 | 0.31 |
| Nitrogen[c] | 25 | 2053 | 5092.274 | −0.1734 | 0.09 | 0.29 |
| Ethylene[d] | 100 | 2269 | 2082.868 | −0.0413 | 0.19 | 0.64 |
| Benzene\*\* | 25 | 868[f] | 2.68806 | 0.33320 | 0.002 | 0.003 |
| Water[†] | 25 | 1500[g] | 4.17917 | 0.66864 | 0.010 | 0.013 |
| Alcohol[†] | 25 | 1500[g] | 3.30631 | 0.31927 | 0.020 | 0.025 |

\* See reference 9.
[a] In all of Keyes and Kirkwood's data the pressures are in atmospheres and the volumes are in liters/mol. The lower pressure limit is in all cases above atmospheric pressure.
[b] Michels and Hammers, Physica 4, 1002 (1937). $\lambda = 5876$A.
[c] Michels, Lebesque, and De Groot, Physica 13, 337 (1947). $\lambda = 5876$A.
[d] Michels, Botzen, and De Groot, Physica 13, 343 (1947). $\lambda = 5876$A.
\*\* See reference 4.
[†] See reference 1.
[e] In all of Michels' data the pressures are in atmospheres and the densities are given in Amagat units; the volumes used in calculating the constants above are the reciprocals of these densities. The lower pressure limit is (except for Nitrogen) the atmospheric pressure.
[f] Pressure in bars. $\lambda = 589$ $m\mu$.
[g] Pressure in atmospheres. $\lambda = 579$ $m\mu$.

term as a compression would be consistent with Tammann's hypothesis that the introduction of a dissolved substance has the same effect upon a solvent as compressing the pure liquid under external pressure.

In Tables I and II the constants $m$ and $b$ of Eq. (3) are given for liquids and gases whose dielectric constants and indexes of refraction have been measured under pressure by various investigators. These constants were determined by the method of least squares by minimizing the sums of the squares of the difference of the observed and computed values of the function $1/f_P$ (the line of regression of $1/f_P$ on $v_P$).

As has already been noted, Danforth[7] plotted the reciprocals of the Clausius-Mosotti expression against the densities, i.e.,

$$\rho_P/f(\epsilon_P) = b''\rho_P + m'', \qquad (6)$$

where $\rho_P$ is the reciprocal of the specific volume $v_P$ and $1/f_P = (\epsilon+2)/(\epsilon-1)$. We prefer the arrangement of Eq. (3) which can more readily be related to the logarithmic form of Eq. (5). Theoretically, Eqs. (3) and (6) are the same, but it must be noted that in practice, because of the change of variables, the least-square method of fitting the best line of Eq. (3) does not give the same line as in fitting Eq. (6). (The line of regres-

sion of $1/f_P$ on $v_P$ is not the same as the line of regression of $\rho_P/f_P$ on $1/v_P$). It can be shown that if instead of assuming observations of equal weights in fitting the line of Eq. (3), we ascribe to the observations the weights $1/v_P^2$ we will obtain the line of Eq. (6). Conversely, with the weights $v_P^2$ the least-square line of Eq. (6) will be the line of Eq. (3).

In practice, the two lines of regression (3) and (6) give essentially the same results for a number of cases tried. Thus, for carbon bisulfide at 75°C (data of Danforth) and for ammonia at 100°C the two line of Eqs. (3) and (6) give values for $\epsilon_P$ whose average and maximum percent deviation from the observed dielectric constants are practically the same.

Danforth observed that the reciprocal of the Clausius-Mosotti function $\rho_P/f_P$ is linear in the density in the case of all polar substances except ethyl ether and the two more simple non-polar substances carbon bisulfide and pentane. This conclusion is not altogether admissible from the results shown in Table I. Ethyl ether does consistently show the greatest deviations from linearity in the data of Chang and Kyropoulos as well as in the work of Danforth. However, the least-square line for pentane is associated with the smallest deviations shown in Table I, while at 75°C carbon bisulfide (Danforth and Chang) fits comparatively well, and at 30°C the results for carbon bisulfide are better than those for ethyl alcohol (0°C), which according to Danforth behaves normally. Evidently, Danforth drew his conclusions on the exceptional behavior of these substances by relying on graphical representation to estimate linearity.

TABLE III. Two least square formulas $1/f_P = mv_P + b$ for the refractive indices of a gas\* for which the range of the function $1/f_P = (n_P^2+2)/(n_P^2-1)$ is extensive. The equation $1/f_P = 3294.03v_P + 0.0363$ was obtained by minimizing the sum of the squares of the difference of the observed from the computed value of the function $1/f_P$. The better fitting equation $1/f_P = 3330.76v_P + 0.1108$ was obtained by minimizing the sum of the squares of the percent difference between the observed and computed values of the refractive indices of the gas. The last two columns show the percent difference between the observed refractive indices and those computed from these equations.

| Pressure. atmos. | $n_{5876}$ | $v_P$\*\* | $1/f_P$ obs'd. | Percent deviation of $n$ | |
|---|---|---|---|---|---|
| 21.35 | 1.0097 | 0.047015 | 154.9250 | 0.002 | 0.010 |
| 49.24 | 1.0278 | 0.016316 | 55.2198 | −0.057 | −0.039 |
| 56.25 | 1.0345 | 0.013101 | 43.2000 | 0.025 | 0.042 |
| 63.35 | 1.0438 | 0.010337 | 34.5121 | −0.012 | 0.004 |
| 67.41 | 1.0512 | 0.008827 | 29.5660 | −0.021 | −0.009 |
| 72.35 | 1.0676 | 0.006691 | 22.4638 | −0.018 | −0.019 |
| 77.92 | 1.1482 | 0.003103 | 10.4232 | 0.208 | 0.030 |
| 86.45 | 1.1642 | 0.002802 | 9.4421 | 0.235 | 0.002 |
| 96.74 | 1.1735 | 0.002655 | 8.9554 | 0.263 | −0.003 |
| 106.46 | 1.1794 | 0.002569 | 9.6730 | 0.278 | −0.010 |
| 121.60 | 1.1864 | 0.002476 | 8.3612 | 0.312 | −0.007 |
| Average percent deviaion of $n$ | | | | 0.130 | 0.016 |
| Maximum percent deviation of $n$, 0.312, 0.042. | | | | | |

\* Carbon Dioxide at 32.075°C. Data of Michels and Hamers, Physica 4, 1002 (1937).
\*\* The volumes shown are the reciprocals of the densities originally given in Amagat units.

TABLE IV. The parameters $A$ and $B$ of the Tait equation $A \log_{10}(1+P/B)$ fitted by the method of least squares to the functions $1/f_0-1/f_P$*, $1/\epsilon_0-1/\epsilon_P$ and the compressions $v_0-v_P$. The three sets of parameters are given for each substance in the foregoing order. The last two columns give the average and maximum percent deviations between the observed and calculated values of $\epsilon_P$. The pressures and volumes are in the units of the original data.

| Substance | $t$°C | $\epsilon_0$ | $P_{max}$ | $A$ | $B$‡ | $(\%)_{av}$ | $(\%)_{max}$ |
|---|---|---|---|---|---|---|---|
| Pentane** | 30 | 1.82 | 12000[b] | 0.9113 | 359 | 0.096 | 0.285 |
| | | | | 0.09106 | 625 | 0.154 | 0.334 |
| | | | | 0.3449 | 354 | 0.113 | 0.511 |
| Glycerine** | 0 | 49.9 | 8000 | 0.02315 | 3807 | 0.051 | 0.098 |
| | | | | 0.07472 | 3826 | 0.063 | 0.163 |
| | | | | 0.1464 | 2845 | 0.134 | 0.190 |
| Carbon bisulfide** | 30 | 2.61 | 12000 | 0.5054 | 610 | 0.186 | 0.544 |
| | | | | 0.08231 | 848 | 0.281 | 0.671 |
| | | | | 0.2005 | 1129 | 0.074 | 0.211 |
| Bromobenzene** | 75 | 4.87 | 8000 | 0.1732 | 936 | 0.121 | 0.242 |
| | | | | 0.03989 | 1049 | 0.124 | 0.268 |
| | | | | 0.1520 | 983 | 0.108 | 0.238 |
| Acetone[b] | 20 | 21.50 | 3000[b] | 0.03911 | 795 | 0.085 | 0.176 |
| | | | | 0.01196 | 799 | 0.087 | 0.177 |
| | | | | 0.3202 | 1085 | 0.077 | 0.229 |
| Carbon tetrachloride[b] | 18 | 2.246 | 1000[b] | 0.8403 | 1144 | 0.009 | 0.020 |
| | | | | 0.1033 | 1376 | 0.010 | 0.023 |
| | | | | — | 934[c] | — | — |
| Ammonia† | 100 | 1.0940[d] | 55 | 28.789 | −14.12[e] | 0.163 | 0.314 |
| | | | | — | —[f] | — | — |
| | | | | 1.2085 | −14.05[e] | 0.675 | 1.167 |
| Benzene†† | 45 | 1.4851[g] | 1188[h] | 0.699133 | 859 | 0.003 | 0.005 |
| | | | | 0.082786 | 1030 | 0.002 | 0.004 |
| | | | | 0.253355 | 829[c] | — | — |

* $1/f_P=(\epsilon_P+2)/(\epsilon_P-1)$. $1/f_0$ is the value of the function at either the atmospheric or the initial pressure.
‡ $B$ is in the same units as the pressure.
** See reference 7.
[b] Atmospheres. All of Danforth's pressures are in this unit.
[b] The data of Kyropoulos. His pressures are in kg/cm².
[c] The value of Gibson.
† See reference 9.
†† See reference 4.
[d] The value at 20 atmos. the lower pressure limit.
[e] The function fitted here is that of Eq. (5) where $m$ and $1/f_0$ are replaced by the values at $P'=20$ atmos. the initial pressure.
[f] The function $1/\epsilon-1/\epsilon_P$ cannot, in this case, be represented by a Tait equation.
[g] The index of refraction $\lambda=589\ m\mu$. $\epsilon_P$ is replaced by $n_P^2$ in the equations.
[h] Pressure in bars.

## WEIGHTED FORMULAS FOR GASES

In the last two columns of Tables I and II are shown the average and the maximum percent difference between the observed and computed value of the dielectric constant or refractive index $(100\Delta n/n)$.[11] This is the criterion used for the closeness of fit of the interpolation formula of Eq. (3), though in fitting this line by the method of least squares, we minimized the sum of the squares of $\Delta(1/f_P)$, the difference of the observed and the computed values of the function $1/f_P$. Obviously, this is not the proper function to minimize to give us the most favorable deviations of $n_P$ (or $\epsilon_P$). Generally, this inconsistency is not serious and it has the advantage of lessening the computational work involved in applying the method of least squares. The parameters $m$ and $b$ shown in Tables I and II were all found by fitting Eq. (3) in this way. However, where the

[11] $\Delta n$ (or $\Delta \epsilon$) will denote the absolute value of the difference between the observed and computed value of $n_P$ (or $\epsilon_P$). The $\Delta$ will have the same significance when used with the function $1/f_P$.

range of the function $1/f_P$ is extensive (e.g., in the case of a gas, see Table III), the simplification of minimizing the sums of the squares of the residuals of $1/f_P$ tends to pile up at the higher pressures large percent differences between the observed and computed values of $n_P$ (or $\epsilon_P$). This is apparent from the second to last column of Table III, where the data for the refractive indices of carbon dioxide are given as an illustrative example. The distribution of percentages in this column resulted from fitting Eq. (3) in the usual way. The last column, however, shows a better distribution of the percent difference between the observed and computed values of $n_P$; in fact, an over-all improvement in fitting the observed values of $n_P$ to Eq. (3) has been affected.

To obtain the distribution of percentages indicated in the last column of Table III, we fit the observed data to Eq. (3) in another manner. Instead of minimizing $\sum\{\Delta(1/f)\}^2$ we minimize $(\sum \Delta n/n)^2$, i.e., the sum of the squares of the percent difference between the observed

and computed values of $n_P$. We assume below that the function $1/f_P$ involves the indices of refraction $n_P$, but obviously the same procedure will apply where the dielectric constants are considered.

If we write the approximate relation

$$\Delta n = \Delta(1/f)/(1/f)',$$

where $(1/f)' = d(1/f)/dn$; then

$$\sum (\Delta n/n)^2 = \sum \{\Delta(1/f)/n(1/f)'\}^2$$

is the new function we must minimize. This is equivalent to ascribing to the function $1/f_P$ a weight $w_P$, which is for each observation given by

$$w = \{1/n(1/f)'\}^2.$$

The published results of most of the investigators whose data we have used do not include enough information to permit a precise comparison with the deviations from our interpolation formula. Danforth, from whom the bulk of our data for very high pressures is taken, gives no estimate of the uncertainties in his measurements. However, with few exceptions, the Eq. (3) will represent his data within a few units in the last significant figure in $\epsilon$. A reasonable estimate of the experimental error of Gibson's measurements of the indices of refraction of benzene is perhaps 0.01 percent, and it may be seen that our interpolation formula reproduces his results well within this experimental error. Keyes and Kirkwood's experimental error for carbon dioxide is about 0.2 percent (and presumably, though they do not indicate this, it may be assumed to be the same for ammonia). Table II shows that we have fitted their data within this experimental error except in the case of carbon dioxide at 35°. But Keyes and Kirkwood point out that they consider Amagat's compressibility data, which they used, unreliable above 60 atmospheres; and here, too, is where our interpolation formula fails. Except in this case and that of the gases discussed below there are no visible trends in the residuals from the interpolation formula for the substances in Tables I and II.

The situation, however, for the refractive index measurements of Michels et al. for carbon dioxide, nitrogen, and ethylene shown in Table II is somewhat different. The average deviations indicated for these gases in Table II are considerably in excess of the general accuracy claimed for their measurements. Furthermore, in the second last column of Table III, where the deviations are enumerated in detail for carbon dioxide, a systematic trend may be observed at higher pressures. However, the last column, which gives the deviations for the weighted formula, shows that this trend has been obliterated. The average percent deviation of $n$ indicated in this column (0.016 percent) is in accord with the accuracy which Michels usually claims, but the maximum percent deviation in $n$ (0.042 percent) may be too high. Considering the difficulties recorded by the

investigators because the measurements pass through the region of the critical point, this abnormal deviation may reflect only this experimental situation.

It may reasonably be claimed that the interpolation formula (3) represents the data for liquids, and that the same weighted formula reproduces the results for gases within the experimental error.

## SIGNIFICANCE OF THE PARAMETER B

Owen and Brinkely[8] conclude that the parameter $B$ in the equation

$$1/\epsilon_0 - 1/\epsilon_P = A \, \log(1+P/B) \qquad (7)$$

has the same value as in the analogous Tait equation for the compressions of the liquid, i.e., the same value of $B$ may be determined independently from either the dielectric constants or the densities. Their evidence for this conclusion is, aside from considerations of electrostatic theory and Tammann's hypothesis, that Eq. (7) accurately reproduces the variations of the dielectric constant with pressure for some liquids with values for $B$ obtained by Gibson[12] from compressibility data. Since, however, it has been shown in this article that it is possible to replace $1/\epsilon$ in Eq. (7) by other functions, and especially the function $1/f = (\epsilon+2)/(\epsilon-1)$, it seemed necessary to investigate more rigorously the nature of the parameter $B$ when it is determined from compressibility as well as dielectric constant data over the *same* range of pressures and with $1/f_P$ as both $(\epsilon_P+2)/(\epsilon_P-1)$ and $1/\epsilon_P$.

Another factor prompts a reconsideration of the significance of the parameter $B$ in these equations. The value of $B$ in the Tait equation is not critical, and as the equation has another disposable constant it is understandable that widely varying values of $B$ in (7) may yet enable the equation to express the isothermal variations of the dielectric constant of liquids with pressure. It is, therefore, not surprising to see values of $B$, determined from compressibility data to pressures of approximately 1000 atmospheres,[13] successfully used by Owen and Brinkely in Eq. (7) to represent dielectric constant data to as high as 12,000 atmospheres. This assumes what is only approximately true, that the parameter $B$ in Tait's equation is independent of the external pressure on the solution. But $B$ is not quite constant for a given liquid but depends on the pressure range of the data.[14] For this reason all values of $B$

[12] Gibson's values of $B$ are summarized by Harned and Owen. See reference 5.

[13] Gibson's values of $B$ were determined from compressibility data in this range. These were applied by Owen and Brinkely to Danforth's data whose maximum pressure range is 12,000 atmos. and to Kyropoulos's data to 3000 kg/cm².

[14] Besides the relevance of this observation here it should also have some bearing in speculation (see reference 4) on the theoretical significance of the parameter $B$ in Tait's equation. This should not only take into consideration the dependence of $B$ on the pressure range but should also consider the manner in which the curve was fitted to the data.

presented here for comparison have been determined from the same pressure range.

In Table IV are given the parameters $A$ and $B$ of $A \log_{10}(1+P/B)$ fitted by the method of least squares to the functions $1/f_0 - 1/f_P$, $1/\epsilon_0 - 1/\epsilon_P$ and to the compressions $v_0 - v_P$. For each substance in the table three sets of the two parameters $A$ and $B$ are given corresponding to the functions given in the above order; the pressure range for these three functions is, for any particular substance, the same.[15]

Generally, it will be observed, the function $1/f_0 - 1/f_P$ fits the data somewhat better than $1/\epsilon_0 - 1/\epsilon_P$, but the values of the parameter $B$ corresponding to these two functions sometimes differ considerably. When $\epsilon_P$ is large (e.g., glycerine and acetone), it may easily be shown by expansion in series that the function $1/f_P$ is approximately linear in $1/\epsilon_P$ so that $1/f_0 - 1/f_P$ is proportional to $1/\epsilon_0 - 1/\epsilon_P$, in which case the parameters $B$ in the logarithmic form of these functions necessarily have nearly the same value (but this value of $B$ is not necessarily the same value of $B$ obtained from the compressibility data).

On the other hand, where the values of $\epsilon_P$ are small (as in pentane) the $B$ in the logarithmic representation of the function $1/\epsilon_0 - 1/\epsilon_P$ does not, if pentane is typical of this class, have even nearly the value of $B$ obtained by fitting the dielectric constant data to the function $1/f_P = (\epsilon_P+2)/(\epsilon_P-1)$.

For ammonia where the values of $\epsilon_P$ are only somewhat larger than one, and for other gases that were tried (where $B$ is negative), the function $1/\epsilon_0 - 1/\epsilon_P$ gives, when plotted against the pressure, a curve that is concave upward, so that it is not possible to represent the function $1/\epsilon_0 - 1/\epsilon_P$ by a Tait equation. However, the function $1/f_P = (\epsilon_P+2)/(\epsilon_P-1)$, as may be seen from Table IV, when adjusted to the data gives a value of $B$ which agrees well with the value of $B$ obtained from the compressibility data.

In conclusion it might be said that the results of Table IV lend some plausibility to the thesis that the parameters $B$ of the logarithmic representation of the function $1/f_0 - 1/f_P$ (and sometimes the function $1/\epsilon_0 - 1/\epsilon_P$) is the same as the $B$ determined by the Tait

equation for $v_0 - v_P$. However, it is evident that more reliable data would be required before this proposition could be established conclusively; for it must be kept in mind that the parameter $B$ is extremely sensitive to very small variations in the data from which it is determined and that small deviations in the measurements affect the value of $B$ enormously.

## THE TAIT EQUATION FOR GASES

As we have shown in Table IV, it has been possible to adjust $v_{P'} - v_P$ and $1/f_{P'} - 1/f_P$ for ammonia at $100°C$ to the Tait function

$$A \log\{(P+B)/(P'+B)\},$$

where $v_{P'} = 1.385$ and $1/f_{P'} = 32.915$, the values corresponding to the initial pressure $P' = 20$ atmos. It has already been pointed out that it is not possible to use the function $1/\epsilon_0 - 1/\epsilon_P$ for gases; and that $B$, unlike that for liquids, is negative.

It may be observed that though the pressure range is relatively small (20–55 atmos.), the compressibility data of ammonia are not reproduced by the Tait equation as well as it is for liquids over greater ranges of pressure. That this is not because the data are inherently less accurate may be indicated by the fact that the ammonia densities used are the measurements of Beattie and Lawrence,[16] who also represented them by an equation of state (over the range 17–58 atmos.) but with somewhat better results. Their maximum percent deviation between the observed and calculated volumes was about 0.8 percent as compared to the 1.17 percent (and 0.68 percent average) shown in Table IV.

It is, however, quite noteworthy that the Tait equation, which can so well be adapted to compressibility data for liquids (and some solids), can also be used with gases.[17] The somewhat inferior results obtained for gases emphasize what has already been pointed out— that the parameter $B$ is not independent of the external pressure, and this dependence is particularly greater for gases as is demonstrated by the results obtained for ammonia and by other gases that were examined.

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[15] The compressibility data used are those given by the investigator. It must be pointed out that though Danforth's work was done in Bridgman's laboratory the densities he used do not always agree with Bridgman's published data. Thus, Bridgman's compressibility data for glycerine would give a much higher value for $B$ than that shown in Table IV, but this value of $B$, too, would be of dubious value since the glycerine Bridgman used is admittedly contaminated with water. P. W. Bridgman, Proc. Am. Acad. Sci. **67**, 11 (1932).

[16] J. A. Beattie and C. K. Lawrence, J. Am. Chem. Soc. **52**, 6 (1930).

[17] It might be of some interest to point out that $v_0 - v_P$ is only the simplest function of the volumes that can be represented by the Tait equation. As in the case of the dielectric constants and refractive indices, other functions of $v_P$ may be used, e.g., the Lorentz-Lorenz function $1/f(kv_P) = (1+2kv_P)/(1-kv_P)$ where $k$ is a constant for which $1-kv_P > 0$.