3. The least coprecipitation of lead is obtained when sodium sulfate is added very slowly to the boiling mixture of barium and lead.

4. Barium sulfate precipitated at room temperature from fairly concentrated ammonium acetate solutions is much more perfect than when precipitated in the absence of acetate. The further perfection of the former precipitate is promoted on aging in a solution containing ammonium acetate.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON, AND THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Influence of Temperature and Pressure on the Volume and Refractive Index of Benzene

BY R. E. GIBSON AND JOHN F. KINCAID

Introduction

The influence of pressure on the refractive index of liquids has been measured in the past by two methods. In the first[1] the refractive index changes produced by small pressure changes of the order of one atmosphere were measured with an interferometer. The initial value of dn/dP was obtained in such experiments but not the effect of pressure on dn/dP. In the second method[2] a steel apparatus for withstanding high pressures was used. It was fitted with glass windows mounted so that the liquid between them formed a 30° prism. The refractive index of the liquid was determined from the angle of the prism and the angle of minimum deviation. Readings were made at pressures up to 13,500 atmospheres. This second method has the disadvantage that the windows are an essential part of the light path and what happens to the optical properties of the glass under such conditions is still quite an open question.

In this paper we shall describe a method which has not been used hitherto for measuring the effect of pressure on the refractive indices of liquids, and give results for benzene. The method has limitations but they are obvious. In order to discuss the specific refraction of benzene under different conditions we shall also include new data on the compressions of benzene at different temperatures together with derived thermodynamic quantities and also the densities and rough values of the compressions of three optical glasses.

Experimental

Our method of measuring the effect of pressure on the refractive index of a liquid consists of adjusting the pressure at a constant temperature so that the liquid has the same refractive index as a piece of optical glass immersed in it. The apparatus is shown diagrammatically in Fig. 1. The window bomb itself already has been described.[3] The benzene was contained in a small vessel provided with plane parallel windows. The opening at the

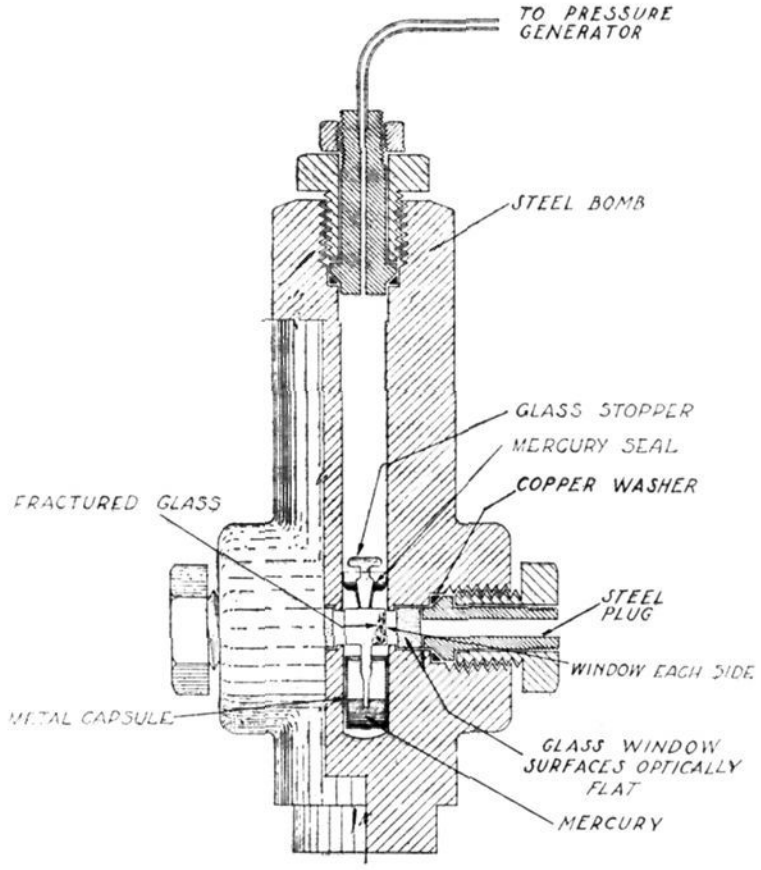

Fig. 1.—Diagram of apparatus for the comparison of the refractive indices of a liquid and a glass under high pressure.

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(1) (a) W. C. Röntgen and L. Zehnder, *Ann. Physik*, **44**, 24 (1891); (b) F. Himstedt and I. Wertheimer, *ibid.*, **67**, 395 (1922); (c) I. Eisele, *ibid.*, **76**, 396 (1925).

(2) T. C. Poulter, C. Ritchey and C. A. Benz, *Phys. Rev.*, **41**, 366 (1932). The effect of pressures up to 1800 atm. on the refractive indices of water, alcohol, and their mixtures, and of carbon bisulfide, has been determined recently, but so far only abstracts of the papers describing this work have been published. See F. E. Poindexter and J. S. Rosen, *Phys. Rev.*, **45**, 760 (1934), and Poindexter, *ibid.*, **47**, 202 (1935).

(3) R. E. Gibson, THIS JOURNAL, **59**, 1521 (1937).

lower end of the vessel was sealed with mercury during an experiment. The vessel also contained fragments of an optical glass whose refractive index was higher than that of the liquid at atmospheric pressure. Monochromatic light entered through one window and through the other the boundaries between the glass and the liquid were observed by means of a microscope. The whole bomb was immersed in a well stirred oil-bath whose temperature was kept constant to within 0.05°. After the bomb and its contents had come to temperature equilibrium, the pressure was raised (care being taken to allow the heat of compression to be dissipated) until the boundaries of an appropriately oriented fragment of glass disappeared. The criterion of match in index between the liquid and the glass was the same as is used in the ordinary determination of the refractive indices of small crystals with a petrographic microscope.[4] With a good source of monochromatic light it was easily possible to reproduce, within 1 bar, the pressure at which the refractive indices matched, a precision corresponding to a change of approximately 0.00004 in the index of the liquid. At all times a change in pressure of 5 bars could be seen to alter the index of the liquid from being definitely below to being definitely above that of the glass. The sensitivity was, therefore, quite satisfactory. The homogeneity of each sample of glass was checked by the observation that all fragments matched with the liquid at the same pressure. Measurements were made with the sodium doublet $\gamma = 589$ mμ and the mercury lines 546 and 436 mμ.

In the experiments recorded here we used three optical glasses taken from a selection kindly placed at our disposal by Mr. G. W. Morey of this Laboratory. Pertinent data concerning these glasses are given in Table I. The specific volumes are the results of new measurements. The compressions are also new but only good to about 10%. The expansion coefficient of glass 522 was taken from the "International Critical Tables"[5] and those of the other glasses were estimated. The composition of glass S. C. 522 is given in the "International Critical Tables."[6] Glass 841 was of approximately the same composition but contained several per cent. more lead oxide. Glass 008 contained 72% SiO_2, 18% Na_2O, 1% Al_2O_3, 5% CaO and 3% MgO.

TABLE I

PROPERTIES OF GLASSES USED IN REFRACTIVE INDEX MEASUREMENTS

Glass number	n_{589} at 25°	n_{546}	n_{436}	$v_{35°}$	$10^4 k_{1000}$ at 35°	$10^6 \alpha$
008	1.5104		1.5212	0.4062	26	(26)
S. C. 522	1.5232	1.5256	1.5360	.3735	26	27
841	1.5311	1.5337	1.5441	.3680	26	(26)

The compressions of benzene to different pressures, approximately 250, 500, 750, 1000 and 1250 bars, were measured in the same bomb with quartz piezometers, following our usual technique.[3] Runs were made at 10° intervals from 25 to 65°. At each temperature three or more independent measurements were made at 1000 bars and at least two at each of the other pressures. While the work was in progress, the electrical resistance pressure gage was recalibrated against a dead-weight gage. The accuracy of the pressure measurements was approximately 1 bar and the precision of the pressure readings lay between 0.5 and 1 bar. The pressure measurements limited the precision of the compression results, as the temperature was controlled to 0.05° and the precision with which the volume changes could be measured was much higher than the precision of the pressure measurements.

Baker and Adamson benzene (Reagent Special) was used after distillation over phosphorus pentoxide at reduced pressure. Precautions were taken to keep air and moisture from the distillate. The specific volumes of the benzene at 25.00 and 30.00° were, respectively, 1.14461 and 1.15165. Recent values given for the specific volume of benzene are 1.14461 at 25° (Wojciechowski),[7] 1.14466 at 25° and 1.15174 at 30° (Pesce),[8] 1.14445 at 25° and 1.15149 at 30° (Cohen and Buij),[9] 1.15149 at 30° (Timmermans and Martin).[10] The density data reassured us that the benzene was sufficiently pure for the work in hand.

Dr. H. E. Merwin found n_D 1.4983 ± 0.0002 at 25.0° for our sample of benzene. This figure agrees with the results of Wojciechowski,[7] n_D 1.49807; Smyth and Walls,[11] n_D 1.49815; and Pesce,[8] n_D 1.49825.

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[4] See, for example, N. H. Hartshorne and A. Stuart, "Crystals and the Polarising Microscope," Edward Arnold & Co., London, 1934, p. 137.

[5] "International Critical Tables," Vol. II, p. 89, Index number **34**.

[6] *Ibid.*, p. 100.

[7] M. Wojciechowski, *Roczniki Chem.*, **16**, 524 (1926); *J. Research Natl. Bur. Standards*, **19**, 347 (1937).

[8] B. Pesce, *Gazz. chim. ital.*, **65**, 440 (1935).

[9] E. Cohen and J. S. Buij, *Z. physik. Chem.*, **B35**, 270 (1937).

[10] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926). Earlier work is reviewed in this last article.

[11] C. P. Smyth and W. S. Walls, THIS JOURNAL, **54**, 1857 (1932).

Results

At all temperatures our compression data may be represented[12] by equations of the form proposed by Tait, namely,

$$k = C \log [(B + P)/B] \qquad (1)$$

In Table II the values of the coefficients C and B in kilobars are given and the differences between the observed and calculated values of k are shown in Fig. 2. Our values of the compressions of benzene are based on the assumptions that the compressibility of silica glass has the constant value 2.76×10^{-6} ml. per ml. per bar over the temperature and pressure range considered[8] and that the specific volume of mercury at different pressures and temperatures might be calculated from the volume-temperature data in the "International Critical Tables"[13] together with the values of the compressibility at different temperatures given by Hubbard and Loomis.[14] Figure 2 shows that our compressions are reproducible within the limits of precision set by the pressure readings, *viz.*, 0.00005 to 0.0001 ml.

TABLE II

COEFFICIENTS IN THE TAIT EQUATION FOR BENZENE AT DIFFERENT TEMPERATURES AND COMPARISON OF THE EXTRAPOLATED COMPRESSIBILITIES AT 1 BAR WITH THOSE DETERMINED DIRECTLY

Temp., °C.	C	B (kilobars)	$10^6\beta$ at 1 bar (calculated)	$10^6\beta$ at 1 bar (F. H. A.)
10		(1.084)	86.5	86.4
20		(1.007)	93.1	93.7
25	0.21591	0.970		
30		(.934)	100.4	101.2
35	.21591	.899		
40		(.863)	108.6	108.6
45	.21591	.829		
50		(.796)	117.8	118.3
55	.21591	.763		
65	.21591	.701		

The experimental observations gave values of the pressures and temperatures at which the refractive index of benzene was the same as that of the immersed glass. In order to estimate the change in the index of the benzene for a given change of conditions, we had to make some assumption about the effect of pressure and temperature on the refractive index of the glass. It was assumed that the refractive index of the glass was, within the limits of these experiments, a function of its volume only and that its change produced by a given rise of pressure and temperature could be calculated from the compressibility and thermal expansibility by one of the well-known refraction formulas. As all these formulas gave practically the same results for a particular sample, we chose the simple Gladstone-Dale equation, *viz.*, $(n-1)v$ = constant. The figures in the second columns of Tables III and IV represent the refractive indices of the glass as calculated in this way, at the different pressures and temperatures at which the benzene and the glasses matched. For a given change in pressure the index of the glass changes about 0.025 times that of the liquid. The correction for the glass is, therefore, not critical.

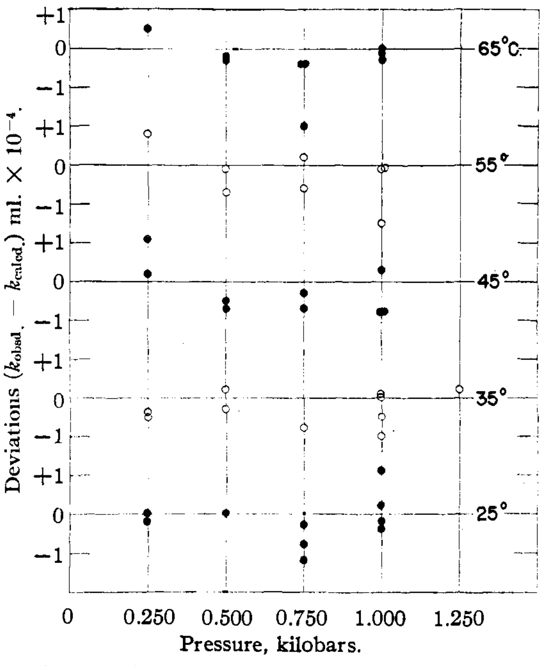

Fig. 2.—Differences between the observed compressions of benzene and those calculated by Tait equations with the constants given in Table II.

Discussion of Results

Pressure-Volume-Temperature Data.—Over the range we have investigated, the Tait equation represents the compression data within experimental error and there are no visible trends in the residuals (Fig. 2). The constants B and C were determined by the method of least squares at 25°, and it was found that the value of C for the

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[12] The symbols used in this paper are: v is the specific volume, P the pressure, t the temperature in °C., T the absolute temperature, k the bulk compression $(-\Delta v/v_0)$ and α the volume coefficient of expansion $1/v_0(\mathrm{d}v/\mathrm{d}T)$. The heat capacities per gram at constant pressure and constant volume are denoted by c_p and c_v, respectively, the internal energy by E. The refractive index is denoted by n with a subscript to denote the wave length of light (λ) used. B and C are the constants in the Tait equation. The differential coefficient $(\mathrm{d}(B + P)/\mathrm{d}T)_v$ is denoted by γ'.

[13] "International Critical Tables," Vol. II, p. 458.

[14] J. C. Hubbard and A. L. Loomis, *Phil. Mag.*, **5**, 1186 (1928).

TABLE III

THE REFRACTIVE INDICES OF BENZENE AT DIFFERENT PRESSURES AND TEMPERATURES AND THE SPECIFIC REFRACTIONS COMPUTED BY THE LORENTZ–LORENZ AND EYKMAN FORMULAS. $\lambda = 589$ mμ

P (bars)	n_{589}	v	Eykman constant	Lorentz–Lorenz "constant"
		25°		
1	1.4983	1.14461	0.7506	0.3357
272	1.5108	1.11819	.7505	.3349
617	1.5240	1.09184	.7506	.3341
868	1.5323	1.07611	.7507	.3336
		35°		
1	1.4918	1.15878	0.7507	0.3361
411	1.5108	1.11798	.7504	.3348
767	1.5241	1.09185	.7507	.3341
1030	1.5324	1.07594	.7507	.3336
		45°		
1	1.4851	1.17343	0.7504	0.3364
547	1.5108	1.11782	.7503	.3348
919	1.5242	1.09149	.7505	.3340
1188	1.5324	1.07574	.7505	.3335

TABLE IV

THE REFRACTIVE INDICES OF BENZENE AT DIFFERENT PRESSURES AND TEMPERATURES AND THE SPECIFIC REFRACTIONS COMPUTED BY THE LORENTZ–LORENZ AND EYKMAN FORMULAS. $\lambda = 436$ mμ

P (bars)	n_{436}	v	Eykman constant	Lorentz–Lorenz "constant"
		25°		
1	1.5201	1.14461	0.7813	0.3480
26	1.5212	1.14186	.7810	.3478
343	1.5365	1.11221	.7816	.3471
561	1.5449	1.09572	.7812	.3464
		35°		
1	1.5134	1.15878	0.7815	0.3485
154	1.5213	1.14171	.7810	.3478
486	1.5365	1.11192	.7814	.3470
713	1.5449	1.09545	.7810	.3463
		45°		
1	1.5065	1.17343	0.7814	0.3489
280	1.5214	1.14158	.7811	.3478
629	1.5366	1.11144	.7812	.3469
867	1.5450	1.09479	.7807	.3461

25° data could be used with an appropriate value of B to express the data at all other temperatures within experimental error. It may be concluded that C is approximately independent of the temperature. Application of the Tait equation to data for other liquids led us to believe that C might not vary with the temperature, but such data had either already been smoothed or showed such scattering that it was impossible to draw any definite conclusions. If C is constant, we know the variation with temperature of the compressibility of benzene when we know B as a function of t. This is given by equation (2)

$$B = 0.970 - 0.00737\,(t - 25) + 0.000016\,(t - 25)^2 \quad (2)$$

With equation (2) and the Tait equation we calculated the compressibilities of benzene at 1 bar pressure at temperatures where they could be compared with those determined from sound velocity measurements by Freyer, Hubbard and Andrews,[15] as is done in Table II. At 20° we also computed the average compressibilities between 100 and 300 bars and between 300 and 500 bars, obtaining 77.9 and 66.8 × 10^{-6}, respectively. From direct measurements Richards, Bartlett and Hodges[16] gave 77.68 and 66.46 × 10^{-6} for these quantities. This good agreement with previous investigators strengthens our confidence in the absolute values of our data.

To determine the specific volumes of benzene at any pressure and temperature we used in addition to the data just discussed the thermal expansion data at 1 bar of Cohen and Buij.[9,17] From their equations we calculated $(v - v_{25})$ and added the results to our own value of v_{25} to obtain the specific volume at any temperature, whence v at any pressure and the same temperature was computed by the relation $(v)_P = (v)_0\,(1 - k)$, the calculated values of k being used.

At different pressures the expansions were expressed by equations of the form

$$(v - v_{25}) = A_1(t - 25) + B_1(t - 25)^2 \quad (3)$$

and the coefficients and residuals are given in Table V.

TABLE V

COEFFICIENTS OF EQUATION 3 GIVING THE THERMAL EXPANSIONS OF BENZENE AT DIFFERENT PRESSURES

P (kilobars)	$10^5 \times A_1$	$10^6 \times B_1$	Deviation × 10^6 Maximum	Deviation × 10^6 Average
0.001	139.1	2.5	2	0.8
.250	120.2	1.1	2	1.5
.500	106.4	0.6	4	2
.750	96.7	.2	5	2
1.000	89.2	.0	4	3

From equation (3) and the coefficients in Table V we may compute the thermal expansion coefficient $(dv/dT)_P$ at different pressures and temperatures and from equations (1) and (2) and the

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(15) E. B. Freyer, J. C. Hubbard and D. H. Andrews, THIS JOURNAL, 51, 759 (1929).

(16) T. W. Richards, E. P. Bartlett and J. H. Hodges, *ibid.*, 43, 1538 (1921).

(17) The expansion data of Cohen and Buij agree excellently with the results of a careful investigation made by J. S. Burlew, now at the Geophysical Laboratory. Dr. Burlew's measurements and equations are not yet published and we thank him for so kindly placing them at our disposal.

coefficients in Table II we may compute $(\mathrm{d}v/\mathrm{d}P)_T$ over the same range by the relation

$$-\left(\frac{\mathrm{d}v}{\mathrm{d}P}\right)_T = \frac{0.4343C}{(B+P)}\,(v)_{P=0}$$

We are thus in a position to calculate with fair accuracy a number of the thermodynamic properties of benzene such as the pressure–temperature coefficient $(\mathrm{d}P/\mathrm{d}T)_v \equiv -(\mathrm{d}v/\mathrm{d}T)_P/(\mathrm{d}v/\mathrm{d}P)_T = (\mathrm{d}v/\mathrm{d}T)_P(B + P)/0.4343v_0C$, the difference between the heat capacities at constant pressure and constant volume, $c_P - c_v = T(\mathrm{d}v/\mathrm{d}T)_P(\mathrm{d}P/\mathrm{d}T)_v$, the coefficient $(\mathrm{d}E/\mathrm{d}v)_T \equiv T(\mathrm{d}P/\mathrm{d}t)_v - P$; and the change of c_P with pressure, $(\mathrm{d}c^P/\mathrm{d}P)_T = -T(\mathrm{d}^2v/\mathrm{d}T^2)_P$.

Our values of $(\mathrm{d}P/\mathrm{d}T)_v$ at 1 bar agree well with those determined directly, considering the extrapolation we have made. For example, at 25 and 35°, respectively, we find 12.6 and 11.9 bars/degree while Westwater, Frantz and Hildebrand[18] found directly 12.4 and 11.6 bars/degree for $(\mathrm{d}P/\mathrm{d}T)_v$. In Fig. 3 we give the values of $(\mathrm{d}P/\mathrm{d}T)_v$ that we have computed as functions of pressure at different temperatures.

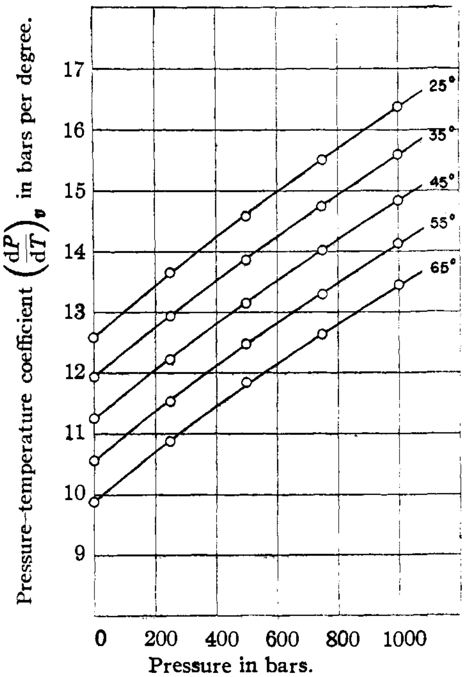

Fig. 3.—The pressure–temperature coefficients of benzene as functions of pressure at different temperatures.

Hildebrand and his colleagues have found that $-v^2(\mathrm{d}E/\mathrm{d}v)_T$ is a constant over a limited range of temperature for non-polar liquids. Our data enable us to examine this function over a much greater range of temperature and pressure than has hitherto been available. The results of our computations, given in Fig. 4, appear to show that $v^2(\mathrm{d}E/\mathrm{d}v)_T$ tends to decrease with rising temperature and rising pressure. On analyzing the apparent temperature trend, however, we find that at 1 bar the average value of $v^2(\mathrm{d}E/\mathrm{d}v)_T$ over the temperature range gives us compressibilities which agree as well with those obtained from the Tait equation as do those of Freyer, Hubbard and Andrews. At 500, 750 and 1000 bars the thermal expansibilities computed from the average values of $v^2(\mathrm{d}E/\mathrm{d}v)_T$ and our compressibilities agree with those we have observed within 0.3%. The temperature trend is, therefore, indicated but not proved beyond doubt by our calculations. There is, however, no doubt that $v^2(\mathrm{d}E/\mathrm{d}v)_T$ varies considerably with pressure. An increase of 1000 bars reduces it by approximately 10% and this is beyond the uncertainties of our calculations or measurements. It must be concluded that over the pressure range we have examined, $v^2(\mathrm{d}E/\mathrm{d}v)_T$ is not constant and $(\mathrm{d}P/\mathrm{d}T)_v$ is not a pure volume function. We noticed that the quantity $\left(\frac{v_0}{v}\left(\frac{\mathrm{d}P}{\mathrm{d}T_v}\right) - P\right)v^2$ varied very little indeed (less than 0.7% from the mean value over the range from 0 to 1000 bars and 25 to 65°).

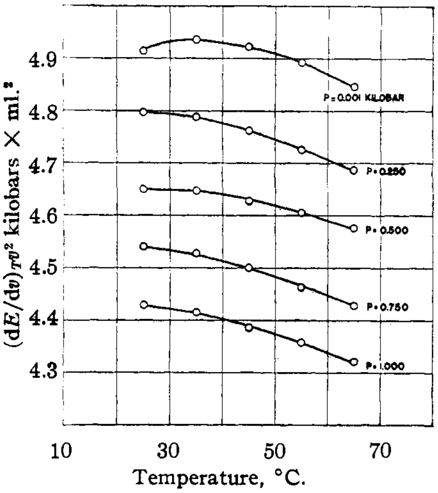

Fig. 4.—The quantity $v^2(\mathrm{d}E/\mathrm{d}v)_T$ at different pressures and temperatures as computed from P–V–T data for benzene.

The coefficient $(\mathrm{d}^2v/\mathrm{d}T^2)_P$ ($2B_1$ in Table V) diminishes with pressure and becomes zero at 1

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[18] N. Westwater, H. W. Frantz and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928).

kilobar. Our pressure range was not sufficiently great to detect the change of sign of $(\mathrm{d}^2v/\mathrm{d}T^2)_P$ which has been found in a large number of liquids between 2 and 3 kilobars.[19]

The Significance of the Constant B in the Tait Equation.—Further analysis of our P–V–T data for benzene has revealed relations which throw light on the physical meaning of the constant B. With the appropriate Tait equations we computed the total internal pressure at constant volume, $(B + P)_v$, at different temperatures between 25 and 65° for various values of the constant volume. We found that equation (4) represented our results within experimental error.[20] Values of γ' for different constant volumes

$$(B + P)_v = -0.860/v^2 + \gamma' T \qquad (4)$$

are given in Table VI. The numerical values of $(B + P)_v$ at 0°K. are the results of a long and hardly justifiable linear extrapolation, but our data warranted no other procedure. The form of the constant term in equation (4) is purely empirical.[21]

TABLE VI

VALUES OF $0.860/v^2$, γ' AND b FOR BENZENE AT DIFFERENT SPECIFIC VOLUMES. SEE EQUATIONS 4 AND 6

v	$0.860/v^2$ (kilobars)	$10^5\gamma'$	b
1.17343	0.626	457.5	0.9406
1.15879	.641	499.6	.9456
1.14461	.657	545.7	.9495
1.12009	.687	639.5	.9536
1.10011	.705	729.7	.9542
1.09	.726	785	.9543
1.08	.738	841.9	.9535

Furthermore, if the slopes of the different isochores are expressed as functions of the volume by the relation $\gamma' = R'/(v-b)$,[22] we find that b is roughly constant, having the values given in Table VI. We may, therefore, represent the family of isochores by the following approximate equation

$$(B + P) = -0.860/v^2 + R'T/(v - b) \qquad (5)$$

which bears a strong resemblance to the equation of state of van der Waals, the chief difference being the presence of the quantity B in equation (5). It should be emphasized, however, that the empirical term $-0.860/v^2$ is not the same as the a/v^2 term in van der Waals' equation. The quantity b reaches a flat maximum in the vicinity of $v = 1.10$. For volume changes of one or two per cent. on either side of this value, b is sufficiently constant to warrant the use of equation (5) for representing the P–V–T data, but outside this range b diminishes too rapidly for this purpose. The decrease of b with decreasing volume may be due in part to the compressibility of the molecules themselves, the decrease of b with increasing volume indicates that the free volume, $(v-b)$, increases more rapidly than does v itself, a conclusion which is plausible when one considers the internal structure of the liquid.

In the light of equation (5) we may use the analysis given by Bridgman[23] and write $P = Tf(v) + \phi(v) + \psi(T)$ for benzene as an example of a liquid, where $Tf(v)$ is the kinetic contribution to the pressure, $\phi(v)$ is the purely volume-dependent part of the internal pressure arising from attractive forces between the molecules, and $\psi(T)$ is B, the temperature-dependent difference between the attractive pressure and the kinetic repulsion (in general a cohesion in liquids), which among other things makes the bulk modulus of a liquid high and, indeed, permits a liquid to remain stable over a considerable range of temperature at atmospheric pressure. It may be added that B must change sign at the critical temperature and that the expansive pressure which balances B arises from the repulsion of the molecules themselves. Since B is a function of the temperature it will be seen at once that Bridgman's conclusion that $(\mathrm{d}P/\mathrm{d}T)_v$ is not a pure volume function is confirmed. The Tait equation assumes that B is independent of the volume and the fact that this equation represents the pressure–volume data so well for a number of liquids appears to justify this assumption. However, the Tait equation in its simplest form does not apply to a number of the more compressible liquids at lower pressures and it seems wise to leave open the question as to whether B is really independent of the volume and to defer any conclusions based on this assumption until more liquids have been examined in detail.

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(19) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**, 227 (1931).

(20) The pressure–temperature curves at constant volume are not linear over the range we have investigated.

(21) Without serious violence to the data we were able to constrain all the straight lines representing $(B + P)_v$ as functions of T to pass through the same point at 0°K. This resulted in an equation of state $(B' + P) = R'T/(v - b)$ which is the same as that proposed by O. Tumlirz [*Sitzber. Wien. Akad. Wiss.*, **118**, IIa, 203 (1909)]. The value of $(B + P)_v$ at 0°K. was taken as -0.700 and from the adjusted slopes, values of b were obtained which varied less with volume than did those obtained from equation (4). Nevertheless equation (5) gave a better representation of the data than the Tumlirz formula.

(22) R' is the gas constant in 10^2 joules per gram per degree.

(23) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**, 229 (1931).

Pressure-Temperature-Refractive Index Relations

The refractive index of a non-polar liquid is generally supposed to be a pure volume function, and for its variation with temperature various formulas giving a specific refraction constant have been proposed. Among others we may mention the Lorentz-Lorenz[24] formula, $v(n^2-1)/(n^2+2)$ = *constant*, the Gladstone-Dale[25] formula, $(n-1)v$ = *constant*, and the Eykman[26] formula, $v(n^2-1)/(n+0.4)$ = *constant*. This last formula is purely empirical and was developed to fit the refractive index-temperature data for organic liquids. We fitted these and other formulas to our refractive index-volume data and only with the Eykman formula was a specific refraction obtained which was independent of pressure and temperature. In columns 4 and 5 of Table III the Eykman constant is compared with the "constant" calculated from the well-known Lorentz-Lorenz formula. A very sensitive test of a specific refraction formula may be made by calculating the compressions of the liquid to various pressures. Previous workers[1] have noted that the compressibilities as computed from the Lorentz-Lorenz or the Gladstone-Dale formulas did not agree with those observed directly. If $F(n)$ denotes that part of the refraction formulas which depends only on the refractive index, then compression to pressure P is obtained by the relation $k = 1 - F(n)_{P=0}/F(n)_P$. In Fig. 5 we have plotted the differences between the observed values of k and those computed from the refractive index changes by different formulas against the observed compressions. The Eykman formula enabled us to calculate the compression of benzene from its refractive index with an error not exceeding 0.5% over a wide range of pressure and temperature. The other formulas are not of much value. From Pesce's[8] data on the refractive index and specific volume of benzene between 25 and 80° we obtained 0.7506 as the average Eykman constant for $\lambda = 589$. This value agrees well with ours which was obtained from absolutely independent data.

On account of difficulties in the visual observations our measurements with mercury blue light ($\lambda = 436$ mμ) were not so precise as those with sodium light. Table IV, however, shows that the measurements of the refractive indices with the mercury blue line are well represented by the Eykman formula, and the compressions calculated from the index changes agree well with those obtained by direct measurement. The measurements with light of wave length $\lambda = 546$ mμ merely confirm the conclusions we have drawn and are not given in detail here.

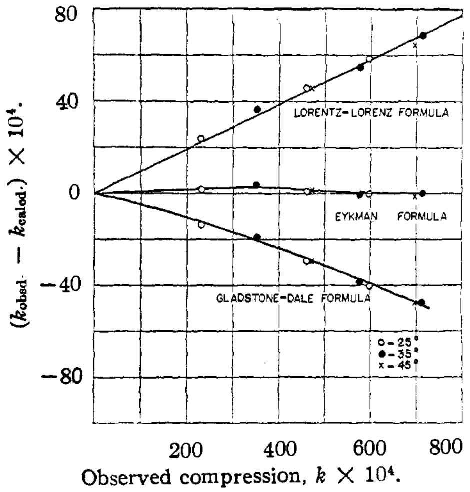

Fig. 5.—Differences between the observed compressions of benzene and those computed from the refractive indices at the same pressures by three specific refraction formulas. The results with the Eykman formula are particularly good. Note that the deviations are functions of the volume only.

Effect of Pressure on the Dispersion of Benzene.—The data of Hubbard[27] and of Timmermans and Martin[10] both show that at 25° and atmospheric pressure $n_{589} - n_{436}$ for benzene is -0.0218. From the Eykman constants and compression data we computed that at 25° and 1000 bars $n_{589} - n_{436} = -0.0235$. Hence the dispersion of benzene increases by approximately 7% per 1000 bars rise in pressure. The dispersion depends only on the specific volume over the range our experiments have covered.

We wish to thank our colleagues G. W. Morey and H. E. Merwin for the interest they have taken in this work and for the material contributions they have made to its progress.

Summary

We have measured the compressions of benzene to different pressures up to 1250 bars at temperatures between 25 and 65°. Our com-

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[24] H. A. Lorentz, *Ann. Physik*, **9**, 641 (1880); L. Lorenz, *ibid.*, **11**, 70 (1880).

[25] J. H. Gladstone and T. P. Dale, *Phil. Trans.*, **153**, 337 (1863).

[26] J. F. Eykman, *Rec. trav. chim.*, **14**, 201 (1895).

[27] J. C. Hubbard, *Phys. Rev.*, **30**, 740 (1910).

pressions are well represented by the Tait equation and the constant C in this equation is independent of temperature. Our results enable us to compute the P–V–T relations and derived quantities with considerable precision over this range of pressure and temperature.

The temperature variation of the constant B in the Tait equation has been studied and B has been fitted empirically into an equation of state of the van der Waals type. Our results indicate that B is the difference between the a/v^2 and $RT/(v-b)$ attractive and repulsive forces in the liquid.

By matching the refractive indices of benzene under different conditions against those of optical glasses we have been able to estimate with considerable accuracy the change of the refractive index of benzene with pressure. Our results confirm the empirical worth of the Eykman specific refraction formula and show that with this formula the compressibility of benzene may be computed from refractive index–pressure measurements almost as accurately as it may be measured directly.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Ammonium Hydroxide on Mercurous Chloride[1]

BY HERTHA R. FRECHE AND M. C. SNEED

Several equations have been formulated to express the reaction which takes place when mercurous chloride is treated with ammonium hydroxide. In 1825, Hennel[2] suggested that the chemical reaction between mercurous chloride and ammonium hydroxide produced mercurous oxide.

Kane and Ullgren[3] suggested the reaction

$$Hg_4Cl_4 + N_2H_6(-H_2Cl_2) \longrightarrow Hg_2Cl_2 + Hg_2N_2H_4$$

According to Rammelsberg[4] and Pesci[5] the reaction occurred according to the equation

$$2Hg_2Cl_2 + 4NH_3 \longrightarrow (Hg_2NCl{\cdot}NH_4Cl + 2Hg) + 2NH_4Cl$$

Barfoed[6] and Saha and Choudhuri[7] proposed the equation

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg + NH_2HgCl + NH_4Cl + 2H_2O$$

Druce[8] introduced the equation

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow NH_2Hg_2Cl + NH_4Cl + 2H_2O$$

Feigl and Sucharipa[9] separated this reaction into the following

$$2NH_3 + Hg_2Cl_2 \longrightarrow NH_2Hg_2Cl + NH_4Cl$$
$$NH_2Hg_2Cl \longrightarrow NH_2HgCl + Hg$$

According to Renz[10] the black substance obtained by the action of ammonium hydroxide on mercurous chloride is mercuric aminochloride and a mercurophotochloride (a stable adsorption product of mercury on mercurous chloride).

Shehigol[11] found that the results of qualitative tests indicated that the reaction between mercurous chloride and ammonium hydroxide is best expressed by the equation

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow [Hg + Hg_2O + NH_2HgCl] + 3NH_4Cl + 3H_2O$$

Thus there is considerable lack of agreement regarding the chemical action of ammonium hydroxide on mercurous chloride. It was thought that this lack of agreement was due to the differences in concentration of the ammonium hydroxide used, as well as to the time of reaction. Therefore, in the present investigation the effects of dilute and concentrated ammonium hydroxide on mercurous chloride and the time of reaction were investigated. It was found that the end-products obtained, when concentrated ammonium hydroxide reacts with mercurous chloride, are a gray precipitate of the composition $Hg + NH_2HgCl$ and the water soluble fusible compound $HgCl_2{\cdot}2NH_3$. In case of dilute ammonium hydroxide, on the other hand, the speed of reaction is sufficiently slow to permit the identification of the intermediate products, namely, mercurous oxide and ammonium chloride, which in turn react to produce mercury and the infusible precipitate, NH_2HgCl.

(1) Based upon a thesis submitted by Hertha R. Freche in partial fulfilment of the requirements for the Ph.D. degree at the University of Minnesota. Original manuscript received July 28, 1931.

(2) Hennel, *The Quarterly Journal of Science, Literature and the Arts*, **18**, 292 (1825).

(3) Kane and Ullgren, *Pogg. Ann.*, **42**, 380–381 (1837).

(4) Rammelsberg, *J. prakt. Chem.*, **138**, 563 (1888).

(5) Pesci, *Z. anorg. Chem.*, **21**, 361 (1899).

(6) Barfoed, *J. prakt. Chem.*, **39**, 211 (1889).

(7) Saha and Choudhuri, *Z. anorg. Chem.*, **67**, 357 (1910).

(8) Druce, *Chem. News*, **123**, 153 (1921).

(9) Feigl and Sucharipa, *Z. anal. Chem.*, **67**, 135 (1926).

(10) Renz, *Helv. Chim. Acta*, **15**, 1316 (1932).

(11) Shehigol, *Ann. chim. anal. chim. appl.*, **18**, 149 (1936).