

## The Refractive Indices of Alcohol, Water, and Their Mixtures at High Pressures

JOSEPH S. ROSEN<sup>1</sup>

University of Kansas City, Kansas City, Missouri

(Received June 30, 1947)

The effect of pressure up to 1800 kg/cm<sup>2</sup> on the refractive indices of ethyl alcohol, water, and five intermediate aqueous solutions of alcohol at 25°C, was measured for the Hg arc lines of wave-lengths 579, 546, 436, and 406 mμ. There is an approximate decrease of 0.6 to 1 percent in the Lorentz-Lorenz "constant," 0.1 to 0.45 percent deviation in the Gladstone and Dale "constant," and 0.2 to 0.6 percent deviation in the empirical Eykman formula. It is concluded that with none of these formulae can the compressions of the solutions be computed from the refractive-index measurements with any great accuracy.

The specific refractions of Gladstone and Dale are found

most suitable for a mixture formula which holds as well through the pressure range of 1500 atmos. as at atmospheric pressure.

Compressions calculated from refraction formulae are found to be a linear function of the observed compressions of the solutions. An equation is given which reproduces with great precision the refractive indices of alcohol, water, and their mixtures; its logarithmic term is the same as that in the Tait equation for compressibilities, and the part containing the refractive indices involves the same function which appears in the formulae of Gladstone and Dale, Lorentz-Lorenz, etc.

THE effect of pressure on the refractive index of liquids had received considerable experimental attention before this century,<sup>2</sup> but no really high pressures were attained until recently.<sup>3</sup> The theoretical Lorentz-Lorenz relation between index of refraction and density,

$$(n^2 - 1)/(n^2 + 2)\rho = \text{constant},$$

has perhaps had its severest experimental trial through the comparison between values for the liquid and vapor states, where the density changed by a factor of as much as 1000. The agreement is surprisingly fair in spite of assumptions that cannot be expected to hold in both states. So, too, where the density is varied by pressure, there is to be expected a slight departure from the Lorentz-Lorenz relation.

The breakdown of the Clausius-Mossotti relation for polar substances led to the Debye-Langevin theory of dipoles and gave stimulus to much recent theoretical and experimental investigations on dielectric constants. Interest in the Lorentz-Lorenz relation, however, has lapsed except insofar as it is incidental to the calculation of electric moments. Similarly, interest in the

mixture laws is primarily due to its relation to the binary solution method of measuring electric moments. The mixture laws of binary solutions give valuable information on the effects of molecules on the refraction of neighboring molecules. At atmospheric pressure the evidence is that intermolecular action upon refraction is negligible.<sup>4</sup> The work in the present paper on the mixture law under pressure extends these conclusions even to conditions where the molecules are brought closer and possibly distorted.

### EXPERIMENTAL

The apparatus employed for measuring the index of refraction at high pressures has already been described;<sup>5</sup> it will only be briefly reviewed here. A heavy steel cylinder is fitted at its two ends with movable parts designed to apply and measure pressure. Prevention of leaks between these units is attained through packing, utilizing the "unsupported area" principle.<sup>2</sup>

In the pressure chamber between the upper and lower movable parts, two narrow slits permit the entry and emergence of light (see Fig. 1). These slits are continued through two movable steel lugs fitted against the inner wall of the pressure chamber. Two flat surfaces on the lugs were available for the mounting of windows.

<sup>1</sup> The experimental part of this paper is the joint work of F. E. Poindexter and the present writer. Only an abstract of the work has been published; this gives the constants of a function of the pressure representing the indices. See F. E. Poindexter and J. S. Rosen, *Phys. Rev.* 45, 760 (1934).

<sup>2</sup> P. W. Bridgman, *The Physics of High Pressure* (The Macmillan Company, New York, 1931).

<sup>3</sup> P. W. Bridgman, *Rev. Mod. Phys.* 18, 75 (1946).

<sup>4</sup> C. P. Smyth, *Dielectric Constant and Molecular Structure* (The Chemical Catalog Company, New York, 1931), p. 159.

<sup>5</sup> W. J. Lyons and F. E. Poindexter, *J. Opt. Soc. Am.* 26, 146 (1936).

With these variable lugs, a maximum prism angle of about  $51^\circ$  was obtainable.

In an apparatus of this size and number of parts, it would have been extremely bothersome, if not impossible, to keep the compressed liquid free from contamination. Consequently, the liquid of which the index was measured was confined to a small rubber sack, with its two ends secured about the periphery of the thick, elliptic-shaped windows. The remainder of the cylinder was filled with glycerine which transmitted the pressure.

The refractive index was determined by the minimum deviation method using the conventional formula. Measurements were made with the lines of the mercury arc spectrum of wavelengths 579, 546, 436, and 406  $m\mu$ .

The refractive indices were measured at room temperature; the thermal effects of compression were effectively minimized by the massiveness of the apparatus and the long intervals between readings. Experiment showed that thermal equilibrium between liquid and apparatus was established in about 10 minutes for the pressure intervals taken in this investigation. It is not probable for this reason that temperatures varied by more than one degree at the time readings were taken. At 2000 atmos. this would affect the index of water by approximately .0001, and by .0002 for alcohol, with intermediate values for mixtures. The refractive indices shown in Tables I and II are the values obtained by adjusting the data to  $25^\circ\text{C}$ , by using experimentally determined values of  $dn/dt$  at various pressures. The refractive indices were measured<sup>1</sup> up to 1800  $\text{kg}/\text{cm}^2$  but are shown here, in 500-atmos. intervals, only to 1500 atmos., since compressibility data for alcohol mixtures are available only to this pressure.

#### COMPRESSIBILITY DATA

The specific volumes of water, ethyl alcohol, and their mixtures have been calculated from the compressibility data of Moesveld.<sup>6</sup> The compressions,<sup>7</sup>  $k_P$ , for the alcohol-water mixtures used in

<sup>6</sup> A. L. T. Moesveld, *Zeits. f. physik. Chemie* 105, 450 (1923).

<sup>7</sup> The symbols used here are:  $k_P$ , the bulk compression, is  $-(v_P - v_0)/v_0$ ;  $v_P$  is the specific volume at pressure  $P$ ;  $\beta_0 = \left(-\frac{1}{v_0} \frac{dv}{dP}\right)_{P=0}$  is the compressibility at  $P=0$  (atmos-

this experiment, and the compressibilities at atmospheric pressure are shown in Table III. The specific volumes at any pressure,  $v_P$ , were computed from the relation  $v_P = v_0(1 - k_P)$ , where  $v_0$  is the specific volume at atmospheric pressure.

The wide applicability of Tait's equation to represent compressibilities of liquids has been shown in recent years,<sup>8</sup> and it is used here to reproduce Moesveld's results.

Tait's equation

$$\frac{dk_P}{dP} = \frac{C}{B+P}, \quad (1)$$

as customarily used, involves two parameters  $C$  and  $B$  both independent of the pressure;  $B$  is a function of the temperature, concentration, and properties of the solution; while  $C$  is approximately independent of the temperature.

From Tait's Eq. (1),  $\beta_P$ , the true compressibility at any pressure  $P$ , is (the temperature remaining constant)

$$\beta_P = \frac{dk}{dP} = -\frac{1}{v_0} \frac{dv}{dP} = \frac{C}{B+P}; \quad (2)$$

so that,  $\beta_0$ , the true compressibility at atmospheric pressure ( $P=0$ ), is  $C/B$ . In the integrated form this equation is

$$k_P = \beta_0 B \ln(1 + P/B); \quad (3)$$

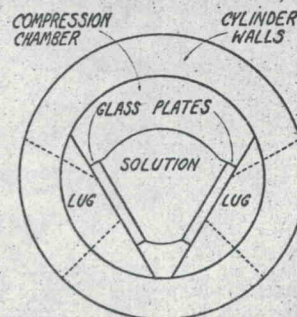


FIG. 1. Cross section of the apparatus used in measuring the refractive indices at high pressures.

pheric pressure);  $n_P$  is the refractive index at  $P$  atmospheres of pressure. The subscript 0 indicates atmospheric pressure. Concentration is expressed in percent by weight.

<sup>8</sup> P. W. Bridgman, *Rev. Mod. Phys.* 18, 17 (1946). See also Harned and Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corp., New York, 1943), p. 270.

where, in this modified Tait's equation, we have set  $C = \beta_0 B$ . For water, alcohol, and their mixtures Moesveld<sup>6</sup> gives for the compressibilities at atmospheric pressure

$$10^6 \beta_0 = 44.5 - .5443c + .01754c^2 - .06585 \cdot 10^{-3}c^3,$$

where  $c$  is the percent by weight of alcohol. Equation (3) is, in this instant, an especially convenient form as it requires the determination of only one parameter  $B$ , a not unimportant advantage when adjusting data to the equation by the method of least squares. Several other points about the relation  $C = \beta_0 B$  are worth mentioning: since  $C$  is independent of the temperature (indeed, varies little for many liquids) the variation of  $B$  with temperature can be calculated if the temperature dependence of  $\beta_0$  is known. Again,

Eq. (3) readily shows how to effect extrapolations for  $\beta_0$  from data at high pressures.

The results of adjusting the observed compressibility data of Moesveld for water, alcohol, and their mixtures to Eq. (3) by the method of least squares are shown in Table III.<sup>9</sup> Figure 2 shows the differences between the observed compressions of the alcohol, water, and their mixtures and those calculated by Tait's equation with the constants shown in Table III. Figure 3 shows the constant  $B$  of Tait's equation plotted against the concentration of the water-alcohol mixtures.

#### MIXTURE LAWS

The molar refraction,  $R_{1,2}$ , of a mixture with two components is defined by the equation<sup>4</sup>

$$R_{1,2} = \frac{(n^2 - 1)v}{n^2 + 2} (f_1 M_1 + f_2 M_2),$$

TABLE I. The refractive indices and the specific refractions of alcohol, water, and their mixtures at different pressures at 25°C.  $\lambda = 579 \text{ m}\mu$  and  $546 \text{ m}\mu$ .

Percent alcohol by weight	Pressure, atmos.	Specific volume	$n_{579}$	Lorentz-Lorenz "constant"		Gladstone-Dale "constant"		$n_{546}$	Lorentz-Lorenz "constant"		Gladstone-Dale "constant"	
				Obs'd.	Calc'd.	Obs'd.	Calc'd.		Obs'd.	Calc'd.	Obs'd.	Calc'd.
Water	1	1.0029	1.3330	.2063		.3340		1.3340	.2069		.3350	
	500	.9818	1.3401	.2059		.3340		1.3413	.2065		.3351	
	1000	.9633	1.3462	.2052		.3335		1.3474	.2059		.3347	
	1500	.9471	1.3516	.2046		.3330		1.3428	.2053		.3347	
19.80	1	1.0345	1.3464	.2205	.2211	.3584	.3586	1.3479	.2214	.2217	.3599	.3597
	500	1.0147	1.3534	.2203	.2207	.3586	.3589	1.3546	.2209	.2214	.3598	.3602
	1000	.9968	1.3592	.2196	.2200	.3581	.3586	1.3605	.2203	.2207	.3594	.3598
	1500	.9815	1.3645	.2190	.2193	.3578	.3580	1.3657	.2197	.2200	.3589	.3598
40.04	1	1.0737	1.3569	.2351	.2362	.3832	.3838	1.3583	.2360	.2369	.3847	.3849
	500	1.0505	1.3653	.2349	.2358	.3837	.3844	1.3665	.2356	.2365	.3850	.3857
	1000	1.0308	1.3720	.2343	.2350	.3835	.3843	1.3731	.2349	.2358	.3846	.3856
	1500	1.0139	1.3776	.2335	.2344	.3828	.3839	1.3787	.2341	.2351	.3840	.3855
60.80	1	1.1298	1.3625	.2509	.2517	.4096	.4096	1.3636	.2516	.2524	.4108	.4108
	500	1.0990	1.3738	.2509	.2513	.4108	.4104	1.3750	.2516	.2521	.4121	.4120
	1000	1.0748	1.3821	.2502	.2505	.4107	.4105	1.3832	.2508	.2513	.4140	.4120
	1500	1.0545	1.3889	.2493	.2498	.4101	.4102	1.3902	.2501	.2505	.4115	.4018
81.30	1	1.1963	1.3634	.2663	.2670	.4347	.4351	1.3645	.2670	.2678	.4361	.4364
	500	1.1547	1.3772	.2657	.2666	.4356	.4362	1.3786	.2666	.2675	.4372	.4379
	1000	1.1241	1.3874	.2649	.2658	.4355	.4365	1.3889	.2658	.2666	.4372	.4380
	1500	1.0994	1.3955	.2639	.2650	.4348	.4363	1.3971	.2648	.2658	.4366	.4378
90.74	1	1.2321	1.3628	.2738	.2741	.4470	.4468	1.3641	.2747	.2749	.4486	.4482
	500	1.1846	1.3779	.2730	.2736	.4477	.4480	1.3795	.2741	.2746	.4496	.4499
	1000	1.1505	1.3890	.2721	.2728	.4475	.4485	1.3901	.2729	.2737	.4488	.4500
	1500	1.1236	1.3980	.2712	.2720	.4472	.4482	1.3992	.2719	.2728	.4485	.4498
Alcohol	1	1.2738	1.3598	.2810		.4583		1.3609	.2818		.4597	
	500	1.2198	1.3769	.2805		.4597		1.3784	.2815		.4616	
	1000	1.1814	1.3895	.2797		.4602		1.3909	.2806		.4618	
	1500	1.1523	1.3992	.2789		.4600		1.4005	.2797		.4615	

<sup>9</sup> The assumption in Tait's equation that  $B$  is independent of the external pressure on the solution is justified by successful adaptation of this equation to compressibility data of many liquids (and some solids). Nevertheless, the values of  $B$  are not constant and depend on the pressure range of the data. Rightly,  $B$  is a function of the pressure.

TABLE II. The refractive indices and the specific refractions of alcohol, water, and their mixtures at different pressures at 25°C.  $\lambda = 436 \text{ m}\mu$  and  $406 \text{ m}\mu$ .

Percent alcohol by weight	Pressure, atmos.	Specific volume	$n_{436}$	Lorentz-Lorenz "constant"		Gladstone-Dale "constant"		$n_{406}$	Lorentz-Lorenz "constant"		Gladstone-Dale "constant"	
				Obs'd.	Calc'd.	Obs'd.	Calc'd.		Obs'd.	Calc'd.	Obs'd.	Calc'd.
Water	1	1.0029	1.3398	.2101		.3408		1.3422	.2115		.3432	
	500	.9818	1.3472	.2097		.3409		1.3496	.2110		.3432	
	1000	.9633	1.3531	.2089		.3401		1.3558	.2104		.3427	
	1500	.9471	1.3588	.2084		.3398		1.3613	.2097		.3422	
19.80	1	1.0345	1.3534	.2245	.2251	.3656	.3659	1.3559	.2260	.2266	.3682	.3685
	500	1.0147	1.3606	.2243	.2247	.3659	.3662	1.3631	.2257	.2261	.3684	.3688
	1000	.9968	1.3665	.2236	.2239	.3653	.3656	1.3691	.2250	.2255	.3679	.3685
	1500	.9815	1.3718	.2230	.2233	.3649	.3654	1.3744	.2244	.2247	.3675	.3680
40.04	1	1.0737	1.3643	.2395	.2405	.3912	.3915	1.3668	.2410	.2421	.3938	.3943
	500	1.0505	1.3727	.2392	.2401	.3915	.3921	1.3753	.2407	.2416	.3943	.3950
	1000	1.0308	1.3794	.2384	.2392	.3911	.3918	1.3820	.2399	.2409	.3938	.3948
	1500	1.0139	1.3852	.2377	.2386	.3906	.3916	1.3879	.2392	.2401	.3933	.3943
60.80	1	1.1298	1.3697	.2554	.2562	.4177	.4177	1.3720	.2568	.2579	.4203	.4208
	500	1.0990	1.3814	.2554	.2558	.4192	.4187	1.3840	.2570	.2575	.4220	.4218
	1000	1.0748	1.3897	.2546	.2549	.4189	.4186	1.3923	.2561	.2567	.4216	.4217
	1500	1.0545	1.3967	.2538	.2542	.4183	.4184	1.3994	.2553	.2558	.4212	.4214
81.30	1	1.1963	1.3705	.2709	.2718	.4432	.4437	1.3734	.2728	.2735	.4467	.4469
	500	1.1547	1.3844	.2702	.2713	.4439	.4450	1.3877	.2723	.2731	.4477	.4483
	1000	1.1241	1.3951	.2696	.2704	.4441	.4450	1.3982	.2714	.2723	.4476	.4484
	1500	1.0994	1.4034	.2685	.2696	.4435	.4449	1.4061	.2701	.2713	.4465	.4481
90.74	1	1.2321	1.3703	.2789	.2790	.4563	.4557	1.3727	.2805	.2807	.4592	.4590
	500	1.1846	1.3857	.2781	.2785	.4569	.4571	1.3888	.2800	.2803	.4606	.4605
	1000	1.1505	1.3965	.2768	.2776	.4562	.4572	1.3993	.2785	.2795	.4594	.4606
	1500	1.1236	1.4058	.2759	.2767	.4560	.4571	1.4087	.2776	.2785	.4592	.4604
Alcohol	1	1.2738	1.3669	.2860		.4674		1.3696	.2878		.4708	
	500	1.2198	1.3844	.2855		.4689		1.3873	.2874		.4724	
	1000	1.1814	1.3971	.2846		.4691		1.4001	.2865		.4727	
	1500	1.1523	1.4071	.2837		.4691		1.4100	.2855		.4724	

in which the  $f$ 's and  $M$ 's refer to the mole fractions and molecular weights, respectively, of the two components. If we replace  $(n^2 - 1)/(n^2 + 2)$  by the expression  $(n - 1)$  introduced by Gladstone and Dale, then  $R_{1,2}$  is sometimes said to define, instead, the molar refractivity. We shall, however, refer to  $R_{1,2}$ , containing either function of  $n$ , as the molar refraction.

Further,

$$R_{1,2} = f_1 R_1 + f_2 R_2,$$

where  $R_1$  and  $R_2$  are the molar refractions of the pure components. It can readily be shown that this equation can be replaced by

$$r_{1,2} = c_1 r_1 + c_2 r_2 = c_1 (r_1 - r_2) + 100 r_2, \quad (4)$$

where the  $c$ 's refer to percent by weight of the components and the  $r$ 's refer to the specific refractions of the mixture and its two components. For convenience in computations Eq. (4), rather

than the equation involving molar refractions and mole fractions, will be used.

The specific refractions for mixtures,  $r_{1,2}$ , both those observed and those calculated by Eq. (4), are shown in Tables I and II, and the agreement between them is good. Thus, it may be said that the specific refraction of a mixture, at any given pressure, is a linear function of the percent of

TABLE III. The compressibilities,  $\beta_0$ , at atmospheric pressure and the compressions,  $k_P$ , for alcohol, water, and their mixtures at 25°C; the parameter,  $B$ , in the Tait equation computed from these data. Pressures are in atmospheres.

Percent alcohol by weight	$\beta_0 \times 10^6$	$k_{500} \times 10^3$	$k_{1000} \times 10^3$	$k_{1500} \times 10^3$	$B$	$2.30259 \beta_0 B$
100.00	100.6	42.4	72.5	95.4	1125	.26060
90.74	90.3	38.5	66.2	88.0	1218	.25334
81.30	80.8	34.8	60.4	81.0	1331	.24762
60.80	61.5	27.3	48.7	66.6	1762	.24930
40.04	46.6	21.6	40.0	55.6	2745	.29453
19.80	40.1	19.2	36.4	51.2	4220	.38955
0.00	44.5	21.1	39.5	55.7	3606	.36949

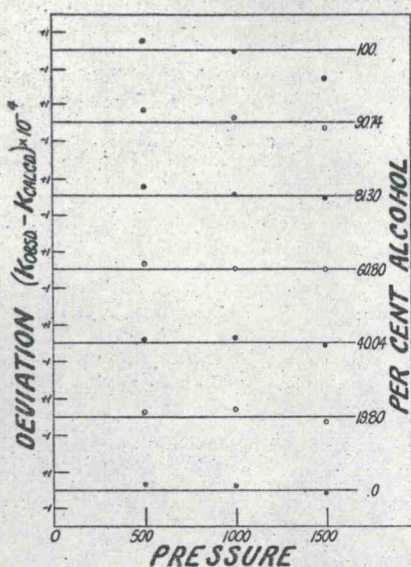


FIG. 2. The differences between the observed compressions of alcohol, water, and their mixtures and those calculated by Tait's equation with the constants shown in Table III.

alcohol (or water)<sup>10</sup> and, therefore, that the specific refractions of the pure components are constant.

Obviously, neither the Lorentz-Lorenz nor the Gladstone and Dale specific refractions remain constant with a change of pressure. In the data shown in Tables I and II there is an approximate deviation of .6 to 1 percent in the observed Lorentz-Lorenz "constant," and from .1 to .45 percent deviation in the Gladstone and Dale "constant." The empirical formula of Eykman,  $(n^2 - 1)v/(n + .4) = \text{"constant,"}$  which so successfully represents the refractive indices of the non-polar liquid benzene<sup>11</sup> to pressures of 1000 bars, was found to be slightly inferior to the Gladstone and Dale formula, but superior to the Lorentz-Lorenz formula. The Eykman "constant" (data not shown) shows deviations of .2 to .6 percent for alcohol, water, and their mixtures.

As a quantitative estimate of how closely the linear relation of Eq. (4) represents the specific

<sup>10</sup> The polarization of solutions of polar liquids such as alcohol and water is not expected to follow Eq. (4). It is, therefore, of interest to remark that Wyman has observed that the polarization of alcohol-water mixtures at 20°C is also very nearly a linear function of the mole fraction of either component. See J. Wyman, Jr., *J. Am. Chem. Soc.* 53, 3301 (1931).

<sup>11</sup> R. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.* 60, 511 (1938).

refractions of the alcohol mixtures, we have proceeded as follows: we substituted into Eq. (4)  $r_{1,2}$ ,  $r_1$ , and  $r_2$ , the *observed* values of the specific refractions (at the same pressure), and calculated the percent of alcohol for each mixture. In Fig. 4 the differences between the actual percent by weight of alcohol and those computed from the observed specific refractions are shown for various pressures. It is evident from this presentation that the linear relation is best approximated, for all pressures, by using the Gladstone and Dale specific refractions instead of the Lorentz-Lorenz refractions in the mixture law of Eq. (4). The same conclusion has previously been reached for these and other mixtures from data at atmospheric pressure.<sup>12</sup> The Eykman specific refractions in Eq. (4), as might be expected from what has previously been said, give calculated values for the concentration of the mixtures that are intermediate to those obtained by using the Gladstone and Dale and the Lorentz-Lorenz refractions.

#### REFRACTIVE INDEX FORMULAE

Of the important formulae for the refractive index of a solution which give a specific refractive "constant," all have the form  $f(n)v = C$ , where  $f(n)$  is a function of the refractive index,  $v$  is the

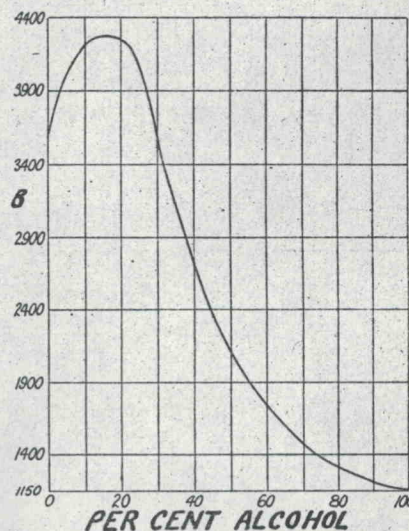


FIG. 3. The constant  $B$  of Tait's equation plotted against the concentration (percent by weight) of the water-alcohol mixtures at 25°C. The values of  $B$  are shown in Table III.

<sup>12</sup> C. Dieterici, *Ann. d. Physik* 67, 337 (1922).

specific volume and  $C$  the "constant." Where the formula is applied to solutions on which the pressure is varied, the expression

$$1 - [f(n_0)/f(n_P)] = k_P' \quad (5)$$

would equal the compression,  $k_P$ , if  $C$  remained constant. Thus the quantity  $k_P - k_P'$ , the difference between the observed compression and that computed from Eq. (5), may be used as a measure in evaluating the worth of the several specific refraction formulae.

By this comparison the advantage generally is with the Gladstone and Dale refractive formula. At 1500 atmos. the compression of water calculated by Eq. (5) is about 5 percent too low by the Gladstone and Dale formula and about 14 percent below the observed value by the Lorentz-Lorenz formula. For alcohol, compressions calculated by either formula deviate as much as 7 percent, but the deviations are opposite in sign. The Eykman formula will reproduce the compressions of alcohol with discrepancies less than 2 percent, but for water the deviations are nearly 10 percent. It must be concluded that none of these formula are of much value for computing the compressions of the solutions of this experiment with any great accuracy.

A more important relation is disclosed on plotting  $k_P'$  of Eq. (5) against  $k_P$ ; the points are collinear. Using the Tait Eq. (3) for  $k_P$ , we express this linear relation by the equation

$$1 - [f(n_0)/f(n_P)] = m \log_{10}(1 + P/B) + b, \quad (6)$$

where  $m$  and  $b$  are constants and  $f(n)$  is the Lorentz-Lorenz expression  $(n^2 - 1)/(n^2 + 2)$ , the Gladstone and Dale expression  $(n - 1)$ , etc.

Some of the constants  $m$  and  $b$  of Eq. (6) were

TABLE IV. The constants  $m$ ,  $m'$ , and  $b$  of Eqs. (6) and (7) for  $\lambda = 579 \text{ m}\mu$ . The parameter  $B$  is shown in Table III.

Percent alcohol	$f(n) = (n - 1)$		$f(n) = (n^2 - 1)/(n^2 + 2)$	
	$m$	$b$	$m$	$b$
100.00	.25644	.00473	.22959	.00432
100.00	.28410*			
90.74	.24351	.00370		
81.30	.23580	.00412		
60.80	.23703	.00467		
40.04	.27303	.00335		
19.80	.35775	.00247		
0.00	.33846	.00191	.30622	.00179
0.00	.37018*			

\*  $m'$  of Eq. (7).

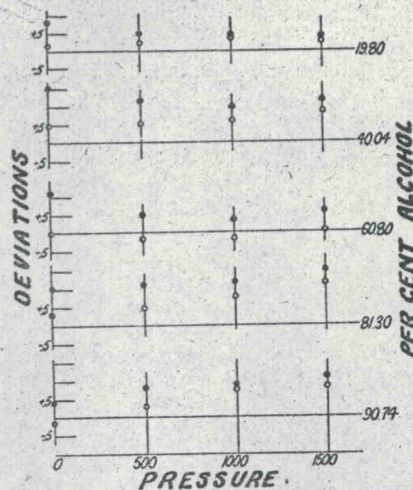


FIG. 4. Differences between the actual percent by weight of alcohol and those computed from the observed specific refractions of alcohol, water, and their mixtures. The circles indicate the deviations obtained by using the Gladstone and Dale refractions in the mixture law; shaded circles indicate deviations obtained by using the Lorentz-Lorenz specific refractions. The Eykman specific refractions give deviations which are approximately intermediate to those shown.

evaluated by the method of least squares and are given for alcohol, water, and their mixtures in Table IV. With these values in Eq. (6), the refractive indices of the solutions are reproduced with great precision for pressures above atmospheric. The values for  $n_P$  obtained from Eq. (6) for water ( $\lambda = 579 \text{ m}\mu$ ) deviate from the observed values given in Table I, at most, by one in the fourth place; the extreme deviation is  $3 \times 10^{-4}$  for alcohol.

A second equation,

$$1 - [f(n_0)/f(n_P)] = m' \log_{10}(1 + P/B), \quad (7)$$

may be used to represent the refractive indices of alcohol, water, and their mixtures at low pressures. This is the line ( $k_P' = m'' k_P$ ) through the origin and through a point on Eq. (6), conveniently chosen at the lowest pressure for which the equation is still considered reliable. Thus, using the results of Eq. (6) for  $P = 500$  atmos., we obtain for alcohol and water ( $\lambda = 579 \text{ m}\mu$ ) the constants  $m'$  of Eq. (7) which are shown in Table IV.

Since direct verification of Eq. (7) for very low pressures is not possible with the data from the apparatus used in this experiment, the values of  $(dn/dP)_{P=0}$  were computed from this equation

and compared with experimental results of previous investigators. For water ( $\lambda = 579 \text{ m}\mu$ ,  $25^\circ\text{C}$ ), Eq. (7) gives the value  $14.8 \times 10^{-6}$  for  $(dn/dP)_{P=0}$ , when  $f(n)$  is both  $(n-1)$  and  $(n^2-1)/(n^2+2)$ . This value agrees exactly with several independent observations.<sup>13-15</sup> This is also the value obtained from the Gladstone and Dale refraction formula with data at atmospheric pressure; and

<sup>13</sup> *International Critical Tables*, Vol. VII, p. 13.

<sup>14</sup> W. C. Röntgen and L. Zehnder, *Ann. d. Physik* 44, 24 (1891).

<sup>15</sup> G. Quincke, *Ann. d. Physik* 19, 401 (1883); *ibid.* 44, 774 (1891).

it confirms the observation of Quincke<sup>15</sup> that the Gladstone and Dale formula represents his experimental results for water at atmospheric pressure.

For alcohol ( $\lambda = 579 \text{ m}\mu$ ,  $25^\circ\text{C}$ ), Eq. (7) gives the value  $39.5 \times 10^{-6}$  for  $(dn/dP)_{P=0}$  when  $f(n)$  is  $(n-1)$ , and essentially the same value when  $f(n) = (n^2-1)/(n^2+2)$ . The available experimental data for alcohol are not in agreement;<sup>15</sup> the value extrapolated from Quincke<sup>15</sup> is about  $37.6 \times 10^{-6}$  and that of Röntgen and Zehnder<sup>14</sup> is  $44 \times 10^{-6}$ .