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THE INTERNAL PRESSURE OF PURE AND MIXED LIQUIDS

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Abstract

Measurement of internal pressures. Defining internal pressure as $T(\partial p/\partial T)_v$, designated $T\gamma$, it can be measured on the principle of a constant volume thermometer. This was done for 8 pure liquids and 12 mixtures of 50 mole percent composition. Values for the former are given at 15°, 20°, 25° and 35°, and for the latter at 20°, 25° and 35°. The values of γ in atmospheres per degree at 20° are as follows: 1 heptane, 8.66; 2 acetone, 11.22; 3 carbon tetrachloride, 11.47; 4 benzene, 12.58; 5 carbon disulfide, 12.67; 6 ethylene chloride, 14.17; 7 ethylene bromide, 15.20; 8 bromoform, 15.32. The values of γ for the mixtures at 20° are, designating the components by the foregoing numbers, 1–2, 9.27; 1–3, 9.68; 1–4, 9.86; 1–5, 9.84; 1–7, 10.66; 1–8, 10.86; 3–4, 12.19; 4–5, 12.32; 4–6, 12.92; 4–8, 14.05; 2–5, 11.77; 5–7, 13.98.

Relations satisfied by $(\partial p/\partial T)_v$.—It was found, further, (1) that γ is a function of the specific or molal volume only; (2) that for each pure liquid $\mathrm{v}^2 T_1 \gamma$ is a constant, a, v being the molal volume, and T_1 the temperature at which the pressure is 1 atmosphere (a function of molal volume); (3) that the values for the mixtures are less than additive, less than those calculated from the equation of Biron, $\gamma = \gamma_1\gamma_2/(\gamma_1\mathrm{N}_1+\gamma_2\mathrm{N}_2)$ where N_1 and N_2 are the mole fractions of the components, here 0.5; (4) that they are given within 1 or 2 percent by the relation $a=(a_1a_2)^{1/2}$ except in some of the mixtures of carbon disulfide, acetone and ethylene chloride—the first of these is in other respects irregular, and the last two are polar; and (5) that a still better agreement is given by considering that $\gamma\mathrm{v}$ is additive.

Indirect determination of compressibility.—The compressibility, β, can be calculated by combining γ with the coefficient of expansion, $\alpha=\beta\gamma$. In most instances, the agreement with the directly determined values is satisfactory.

Introduction

An IDEAL solution has been defined by Lewis and Randall[1] as one in which the fugacity of each constituent is proportional to its mole fraction at all temperatures and pressures. One of us has shown[2] that a consequence of this definition is that only those liquids which have identical values for the change in pressure with temperature at constant volume, $(\partial P/\partial T)_V$, can form such an ideal solution. Calling $T(\partial P/\partial T)_V$ internal pressure, it is therefore evident that differences in internal pressure may account, at least in part, for deviations from ideality. Further progress in the direction of a more quantitative treatment of the deviations, for example, by the integration of an equation given in Ref. 2, p. 68, seems to require more data regarding the variation in internal pressure with the composition of the mixture. The present investigation was undertaken to this end.

Method and Procedure

The direct measurement of $(\partial P/\partial T)_V$, which we will denote by γ, involves the use of what is essentially a constant volume thermometer. Liquid in a

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[1] Lewis and Randall, Thermodynamics. McGraw-Hill Book Co., 1923, p. 221.

[2] Hildebrand, J. Am. Chem. Soc. **43,** 500 (1921); Solubility, Chem. Catalog Co., 1924 Chap. VI.

tube provided with a capillary stem was subjected to a measured increase in temperature and pressure was applied sufficient to keep its volume constant.

The bulb was of Pyrex, about 45 cm long and holding about 65 cc. The capillary stem had an internal diameter of less than 1 mm. In the earlier work carried out by the first named author, the apparatus was arranged as shown in Fig. 2. In the later work, under the second named, the arrangement was that shown in Fig. 1, where, instead of adjusting the mercury to a visible mark on a protruding and fragile capillary, an electrical contact was used. A solid Pyrex rod sealed to the upper end of the tube served as a support for the tube in the apparatus, and also as a means of introducing an electrically insulated lead of fine tungsten wire. It was found to be quite easy to soften an ordinary Pyrex tube into a solid rod about the tungsten wire so tightly that the tungsten-glass union showed no evidence of a leak under a pressure of 25 atmospheres. To this tungsten wire was gold-soldered a rather fine platinum wire which was anchored to the wall of the tube near the bottom to give it rigid support, and which terminated in a fine point just within the capillary, as shown in Fig. 1(b).

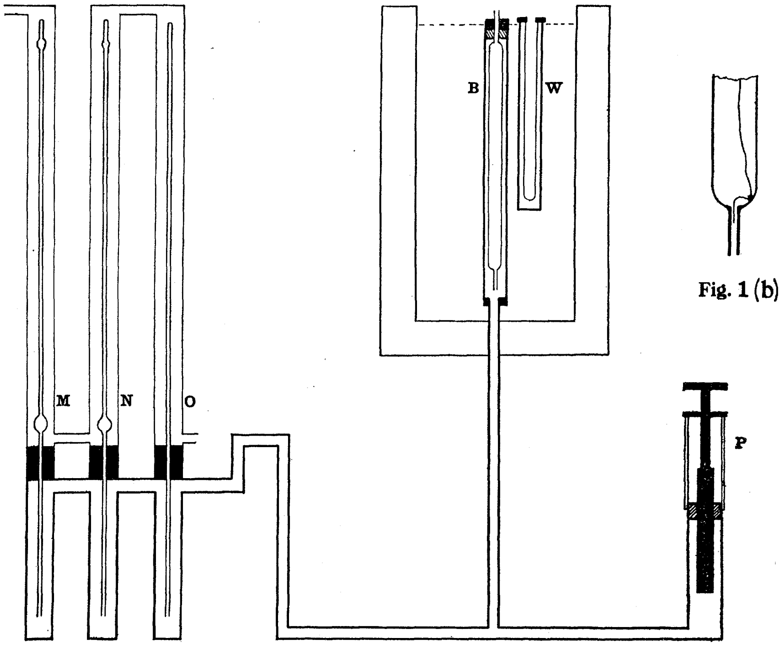

Fig. 1 (b)

Fig. 1(a)

Fig. 1. Diagram of apparatus used in the later work.

The bulb was encased in an hydraulic pipe and surrounded by mercury at the same pressure as that applied to the liquid inside, and the whole fitted into a water thermostat kept at constant temperature by regulating the heat input. The thermostat was shielded from air currents by means of a wooden box. The temperature was measured by a platinum resistance thermometer held in a duplicate bomb (*W*, Fig. 1) in which the pressure remained constant. This bomb served to give the same lag to the resistance thermometer as to the bulb, so that they should not respond unequally to changes in temperature. The resistance was obtained at room temperature by the use of a Leeds and Northrup precision bridge and corrected to 25° with the temperature coefficient of manganin given by Somerville.[3]

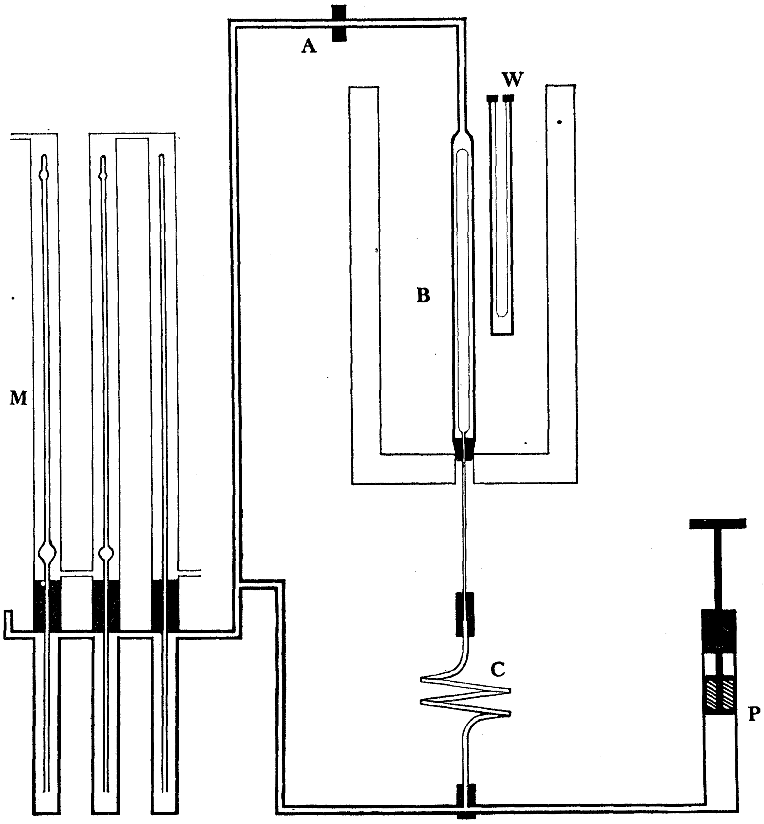

Fig. 2. Diagram of apparatus used in earlier work.

The resistance thermometer, which was capable of being read to 0.001°, was calibrated at the melting point of finely crushed ice, the boiling point of water and the transition point of $Na_2SO_4 \cdot 10\ H_2O$. The salt was recrystallized nine times from the C. P. commercial product.

The pressure was obtained by the use of a mercury screw pump (*P*, Fig. 1) which was packed with oiled leather and gutta percha washers. The pressure was measured by means of three nitrogen filled Amagat manometers (*M*, *N*, *O*, Fig. 1) kept at constant temperature by circulating water from a thermo-

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[3] Somerville, Phys. Rev. **31**, 261 (1910).

stat with a small gear pump. The three manometers were designed to cover different ranges. They were calibrated by comparison with an open-tube mercury manometer constructed of six-foot lengths of iron pipe, added on to the manometer in sections as the measurements were taken, with a section of glass tubing at the end so that the mercury could be read accurately. Readings were taken about every one-half atmosphere. The mercury heights in the gauges were read with a cathetometer, and in the open tube manometer with a calibrated steel tape. The calibration was made to an accuracy of 0.01 atmosphere up to a total of 24 atmospheres. The readings on the manometers were plotted against pressure on a scale sufficiently large to permit pressure to be read to 0.01 atmosphere.

The apparatus was constructed of extra-heavy hydraulic pipe except for the packing glands, which were made of soft steel. The capillary, in the first series, was joined to the pressure system by means of a packing gland and a flexible copper coil which had been lined with rubber. The coil lasted about a year before breaking and then the break was caused by handling and not by amalgamation.

The bulb was sealed to a special distilling apparatus, and in the case of the pure liquids was filled by evacuating and distilling the liquid over phosphorus pentoxide directly into it. In the case of mixtures, these were previously made up by weight to an accuracy of about 0.1 percent, and the tube filled in a manner which prevented evaporation of the mixture, taking care also that air bubbles were not trapped in the tube. The tube was then cooled slightly with ice, disconnected from the distilling apparatus, a small cup of clean mercury fastened to the open capillary end, and the whole placed in the mercury well. The mercury system was then closed by a heavy rubber washer and steel nut. Upon applying pressure to the system, the the liquid in the bulb was compressed and mercury rose in the capillary. Constant volume was maintained by the aid of a mark on the capillary in the first series and by electrical contact in the second, using a microphone hummer and a telephone receiver.

The run was started with the pressure at about twenty to twenty-four atmospheres and the temperature such that a slight increase in pressure closed the telephone circuit. Final adjustment of the pressure was made by expanding the mercury in the pump with an electrical heater placed nearby, until contact was made. At the same instant the pressure indicated by the gauges was read off with the cathetometer, and the temperature of the thermostat was read immediately thereafter. The pressure and temperature readings were then repeated, both as a check on the readings and to make sure that temperature and pressure equilibrium had been established. Ice was added to the thermostat to lower the temperature from 0.1° to 0.2°, and, after a ten minute interval to permit equalization of the conditions, the measurements were repeated. This was continued until the pressure was down to one or two atmospheres. In one case the temperature was again increased, and measurements taken in the higher pressure and temperature range. These values were consistent with the others taken with decreasing temperature.

The temperature was then raised about five degrees, allowing the excess liquid due to expansion to spill out into the mercury system, and the series of measurements repeated. Four such runs were made for each liquid at approximately 20°, 25°, 30°, and 35°.

The pressure was read to an accuracy of 0.01 atmospheres, over a twenty atmosphere range, and the temperature to an accuracy of 0.001°C over about a two degree range for each run. The graph of pressure against temperature showed a strictly linear relationship, the individual points seldom varying more than 0.03 atmosphere from the line. The pressure-temperature coefficient for each run should, therefore, be accurate to about 0.03 atmosphere per degree. The variations in the value of the constants a in Table I indicate that we can claim conservatively an accuracy of 0.5 percent for the smoothed out results.

A correction is necessitated by the fact that the volume of the glass vessel is not strictly constant. When the temperature is increased by ΔT and the pressure by $\Delta p_{\text{obs.}}$, the change in internal volume of the glass, $\Delta v = v\alpha'\Delta T - v\beta'\Delta p_{\text{obs.}}$, where α' and β' are the coefficients of expansion and compressibility of the glass. If Δv were 0, $\Delta p_{\text{obs.}}/\Delta T$ would give the true value of γ, but since this is not the case, extra pressure, $\Delta p - \Delta p_{\text{obs.}}$ would have to be applied to the liquid contents to compensate for Δv, i.e., $\Delta p - \Delta p_{\text{obs.}} = \Delta v/v\beta$, where β is the coefficient of compressibility of the liquid. This gives $\Delta p - \Delta p_{\text{obs.}} = \alpha'\Delta T/\beta - \beta'\Delta p/p$. Dividing through by ΔT and setting $\Delta p/\Delta T = \gamma$, and $\Delta p_{\text{obs.}}/\Delta T = \gamma_{\text{obs.}}$, we obtain $\gamma = \gamma_{\text{obs.}}(1 - \beta'/\beta) + \alpha'/\beta$.

The value α' for Pyrex glass is 1.08×10^{-5} at 20°, according to Buffington and Latimer.[4] The compressbility, according to Bridgman,[5] is 3.06×10^{-6}, using the atmosphere as the unit of pressure. The values of β are in general not known for the mixtures used, so we have simply assumed the mean compressibility of the components, which doubtless suffices for the purpose of the correction.

The heptane, benzene, carbon tetrachloride, and carbon bisulphide were purified by the methods used by previous workers in this laboratory.[6] In each case the boiling point was constant within 0.1°δ when the substances were distilled shortly before use. Kahlbaum's bromoform, and the Eastman Kodak Company's ethylene bromide were each shaken with sodium carbonate solution, washed with water, dried with calcium chloride for 36 hours, and then subjected to three fractional crystallizations, after which the bromoform had a melting point of 7.8°C constant within 0.1°, and the ethylene bromide had a melting point of 9.5°C constant to 0.05°δ. Kahlbaum's acetone prepared from the bisulphite compound was dried with calcium chloride and redistilled, the boiling point being constant to 0.05°δ. The ethylene chloride used was the middle portion from a single fractionation of the Kahlbaum material which boiled within 0.1°.

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[4] Buffington and Latimer, J. Am. Chem. Soc. **48,** 2305 (1926).

[5] Bridgman, Am. J. Sci. [5] **10,** 359 (1925).

[6] Hildebrand and Jenks J. Am. Chem. Soc. **42,** 2181 (1920); Hildebrand and Buehrer Ibid. **42,** 2213 (1920).

The liquids were selected so as to show a wide range in γ, and were mostly of low polarity. Acetone was introduced to have one highly polar substance, and ethylene chloride as one of moderate polarity.

Table I gives observed values of γ as determined by the slopes of the plots of values of p against t, made carefully on a large scale. The linear relationship between p and t is very striking, showing γ to be a function only of the specific or molal volume of the liquid. The table gives values for the molal volume, v, calculated from the temperature at which the pressure is 1

TABLE I

Values of γ for pure liquids.

Liquid	Series	No. obs.	t_1	γ		v	$\gamma T_1 v^2 \cdot 10^{-4}$	Mean
				obs.	correc.			
Heptane	1	10	19.18	8.85	8.73	146.51	5484	
	2	8	19.61	8.87	8.75	146.57	5502	
	2	9	24.19	8.60	8.48	147.42	5479	
	1	9	24.85	8.47	8.36	147.54	5423	
	2	8	28.74	8.33	8.22	148.26	5451	
	1	8	30.19	8.23	8.12	148.53	5435	
	2	8	34.11	8.07	7.96	149.27	5448	
	1	9	36.08	7.95	7.85	149.65	5435	5457
Acetone	2	7	19.04	11.60	11.39	73.19	1782	
	2	7	24.27	11.39	11.19	73.77	1811	
	2	7	29.26	10.81	10.61	74.32	1773	
	2	8	33.38	10.60	10.41	74.77	1784	1788
Carbon tetrachloride	1	9	16.29	12.01	11.75	96.06	3136	
	1	9	23.24	11.50	11.25	96.88	3129	
	1	10	28.98	11.15	10.92	97.54	3128	
	1	10	32.40	10.88	10.66	98.07	3132	3131
Benzene								
	1	13	17.49	13.18	12.87	88.55	2933	
	1	12	25.39	12.46	12.17	89.40	2903	
	1	12	31.81	12.00	11.73	90.11	2904	
	1	11	40.64	11.40	11.15	91.11	2903	2911
Carbon disulfide	1	12	18.64	13.05	12.73	60.19	1345	
	1	10	25.60	12.50	12.19	60.68	1341	
	1	11	30.66	12.20	11.91	61.05	1347	
	1	9	35.71	12.03	11.74	61.44	1368	1350
Ethylene chloride	1	11	17.99	14.78	14.42	78.25	2570	
	1	10	25.12	14.34	13.91	78.89	2582	
	1	7	28.95	13.86	13.44	79.23	2549	
	1	9	33.93	13.71	13.30	79.68	2592	2573
Ethylene bromide	2	6	19.46	15.83	15.19	86.05	3291	
	2	6	24.26	15.47	14.84	86.45	3298	
	2	6	28.38	15.17	14.57	86.80	3309	
	2	6	32.88	14.83	14.25	87.17	3313	3303
Bromoform	1	10	16.21	16.46	15.63	87.17	3436	
	1	7	22.63	15.92	15.12	87.70	3439	
	1	7	28.66	15.32	14.55	88.20	3416	
	1	7	36.38	14.87	14.14	88.87	3456	3437

atmosphere by the aid of the densities given in the International Critical Tables and the coefficients of expansion given in Landolt-BörnsteinTabellen.

It is interesting, of course, to inquire into the functional relation between γ and v. The van der Waals equation,

$$p+a/\mathrm{v}^2=RT/(\mathrm{v}-b)$$

may be compared with the thermodynamic equation of state

$$p+\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V,$$

which suggests trying $\gamma=R/(\mathrm{v}-b)$. This we found to be altogether unsatisfactory, due undoubtedly to lack of constancy of b. The use of some more cumbersome equation expressing b in terms of two or more empirical constants seemed hardly worth while. However, the term a/v^2 seems to be much more satisfactory, for letting $T=T_1$, the temperature at which $p=1$, we have $a=\mathrm{v}^2(T_1\gamma-1)$. The 1 can be neglected, giving $a=\mathrm{v}^2T\gamma$. This may not appear to indicate that γ is a pure function of v, but it must be remembered that when $p=1$, $\mathrm{v}=f(T_1)$. We retain the term T_1 as the expression is much more convenient in this form than it would be if we should eliminate T_1 by the aid of some empirical expression connecting v and T_1.

TABLE II

Smoothed out values of γ for pure liquids.

Liquid	$\gamma T_1 \mathrm{v}^2 \cdot 10^{-4}$		15°	20°	25°	35°
Heptane	5457	v	145.76	146.66	147.57	149.44
		γ	8.93	8.66	8.41	7.93
Acetone	1788	v	72.76	73.71	73.85	74.96
		γ	11.72	11.22	11.00	10.33
Carbon tetrachloride	3131	v	95.92	96.48	97.07	98.28
		γ	11.81	11.47	11.15	10.52
Benzene	2911	v	88.30	88.82	89.34	90.70
		γ	12.95	12.58	12.23	11.49
Carbon disulfide	1350	v	59.95	60.27	60.63	61.38
		γ	13.04	12.67	12.31	11.63
Ethylene chloride	2573	v	78.02	78.72	78.86	79.80
		γ	14.67	14.17	13.88	13.11
Ethylene bromide	3303	v	85.69	86.10	86.51	87.36
		γ	15.61	15.20	14.80	14.05
Bromoform	3437	v	87.06	87.48	87.91	88.78
		γ	15.74	15.32	14.92	14.15

Table I shows the constancy of a to be very satisfactory. We have, therefore, used the mean values of a to calculate values of γ at the even temperatures 15°, 20°, 25° and 35°, given in Table II.

This procedure was impossible, however, in the case of the liquid mixtures, given in Table III, due to lack of figures for the densities and coefficients of expansion. We, therefore, smoothed out the results by plotting log γ against T_1 which should give nearly a straight line. Table III contains the smoothed out values for 20°, 25° and 35°.

TABLE III

Values of γ for 50 mole percent mixtures.

Heptane	t.	19.59	25.60	31.27	36.06	20.00	25.00	35.00
Acetone	Obs.	9.46	9.13	8.80	8.53			
	Correc.	9.28	8.98	8.66	8.39	9.27	9.00	8.47
Heptane	t.	18.75	24.69	30.67	37.32			
Carbon tetra-	Obs.	9.93	9.53	9.26	8.78			
chloride	Correc.	9.76	9.37	9.11	8.64	9.68	9.38	8.79
Heptane	t.	18.16	23.99	28.50	35.02			
Benzene	Obs.	10.05	9.78	9.44	9.28			
	Correc.	9.87	9.60	9.27	9.12	9.86	9.59	9.06
Heptane	t.	19.82	24.98	30.45	34.96			
Carbon disulfide	Obs.	10.04	9.73	9.43	9.03			
	Correc.	9.85	9.55	9.26	8.87	9.84	9.55	8.99
Heptane	t.	17.78	24.95	33.06	40.56			
Ethylene	Obs.	11.10	10.57	10.07	9.70			
bromide	Correc.	10.84	10.33	9.85	9.49	10.66	10.35	9.76
Heptane	t.	20.41	25.88	—	—			
Bromoform	Obs.	11.11	10.81	—	—			
	Correc.	10.84	10.55	—	—	10.86	10.60	10.08
Benzene	t.	17.42	24.78	31.06	37.12			
Carbon tetra-	Obs.	12.67	12.01	11.54	11.20			
chloride	Correc.	12.37	11.74	11.28	10.95	12.19	11.73	11.06
Benzene	t.	17.70	23.96	30.25	36.26			
Carbon disulfide	Obs.	12.78	12.37	11.96	11.53			
	Correc.	12.47	12.07	11.68	11.26	12.32	12.00	11.38
Benzene	t.	17.25	24.11	29.68	35.81			
Ethylene	Obs.	13.46	13.03	12.73	12.39			
chloride	Correc.	13.09	12.67	12.39	12.06	12.92	12.64	12.10
Benzene	t.	17.64	23.77	28.24	—			
Bromoform	Obs.	14.70	14.28	13.90	—			
	Correc.	14.20	13.81	13.44	—	14.05	13.70	13.01
Carbon	t.	18.51	22.40	28.24	32.59			
disulfide	Obs.	12.13	11.85	11.45	11.15			
Acetone	Correc.	11.87	11.60	11.21	10.92	11.77	11.42	10.76
Carbon	t.	18.51	23.67	28.36	32.54			
disulfide	Obs.	14.55	14.12	13.74	13.39			
Ethylene	Correc.	14.10	13.69	13.32	12.98	13.98	13.58	12.81
bromide								

The main problem could now be approached, that of the relation between the values of γ for the pure liquids and for their mixtures. Table IV gives again the values for the pure liquids at 25°, and in the third column of figures, the observed values for the mixtures. In the fourth column are values for the mean, which are, in nearly all cases, greater than the observed values. The deviation from additivity in column five is, in general, greater the greater the difference between γ_1 and γ_2. In the sixth column are figures calculated from an empirical expression of Biron,[7] $\gamma = \gamma_1\gamma_2/(\gamma_1\mathrm{N}_1 + \gamma_2\mathrm{N}_2)$, where N_1 and N_2 are the mole fractions of the liquids in the mixture, here 0.5. It can be seen that while the agreement with the observed values is better than in the preceding column, it is still unsatisfactory.

TABLE IV

Comparison of observed and calculated values of γ for mixtures at 25°.

	γ_1	γ_2	Obs.	Mean	Diff.	Biron	Diff.	$a=(a_1a_2)^{1/2}$	Diff.	Additivity of γv	Diff.
1. Heptane-acetone	8.41	11.00	9.00	9.71	0.71	9.53	0.53	8.55	−0.45	9.27	0.27
2. Heptane-carbon tetrachloride	8.41	11.15	9.38	9.78	0.40	9.59	0.21	9.27	−0.11	9.50	0.12
3. Heptane-benzene	8.41	12.23	9.59	10.32	0.73	9.97	0.40	9.53	−0.06	9.85	0.26
4. Heptane-carbon disulfide	8.41	12.31	9.55	10.36	0.81	10.00	0.45	8.40	−1.15	9.55	0.00
5. Heptane-ethylene bromide	8.41	14.80	10.35	11.61	0.26	10.73	0.38	10.40	+0.05	10.77	0.42
6. Heptane-bromoform	8.41	14.92	10.60	11.67	0.07	10.76	0.16	10.48	−0.12	10.84	0.24
7. Benzene-carbon tetrachloride	12.23	11.15	11.73	11.69	−0.04	11.67	−0.06	11.66	−0.07	11.67	−0.06
8. Benzene-carbon disulfide	12.23	12.31	12.00	12.27	0.27	12.27	0.27	11.82	−0.18	12.26	0.26
9. Benzene-ethylene chloride	12.23	13.88	12.64	13.06	0.42	13.00	0.36	12.98	+0.34	13.00	0.36
10. Benzene-bromoform	12.23	14.92	13.70	13.58	−0.12	13.44	−0.26	13.51	−0.19	13.56	−0.14
11. Carbon-disulfide acetone	12.31	11.00	11.42	11.66	0.24	11.62	0.20	11.52	+0.10	11.59	0.17
12. Carbon-disulfide-ethylene bromide	12.31	14.80	13.58	13.56	−0.02	13.44	−0.14	13.08	−0.50	13.77	0.19
	Mean square of difference				0.192		0.099		0.167		0.066

In the eighth column are calculated values for γ, calculated upon the basis so often used in van der Waals theory that $a = (a_1a_2)^{1/2}$. This gives $\gamma = \mathrm{v}_1\mathrm{v}_2(\gamma_1\gamma_2)^{1/2}/\mathrm{v}^2$, where v is the molal volume of the mixture. For the systems here used, this is probably slightly more than additive. Values given in Ref. 2, p. 63, show that the expansion on mixing is usually less than 1 percent. We may, therefore, write as an approximation

$$\gamma = 4\mathrm{v}_1\mathrm{v}_2(\gamma_1\gamma_2)^{1/2}/(\mathrm{v}_1 + \mathrm{v}_2)^2.$$

The values so calculated are fairly satisfactory, except in the cases involving carbon disulfide. It should be noted, however, that since the calculated values are generally less than the observed, the use of the true molal volumes for the mixtures would make the agreement worse.

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[7] Biron, J. Rus. Phys. Chem. Soc. **44**, 1264 (1912).

The last two columns represent the agreement shown by calculatedvalues for γ upon the basis of additivity of $v\gamma$. The results are usually somewhat larger than the observed. The agreement would be better if we could use the actual molal volumes for the mixtures instead of the mean molal volumes. This method gives the least average departure, as shown by the smallest mean square deviation. We find, as would be expected, that the mixtures containing a polar constituent show a less satisfactory agreement.

Since the linear nature of the relation between p and T for liquids assists greatly in its accurate determination, it offers a means for the indirect determination of the compressibility, β, by aid of the coefficient of expanison, α, through the relation $\beta = \alpha/\gamma$. Table V gives values so calculated, together with some directly observed values. In the case of bromoform, the uncertainty in the observed value of α makes it logical to use the probably rather accurate values of γ and β to correct the value for α.

TABLE V

Compressibility at 1 atmosphere and 20°.

Liquid	γ	$\alpha \times 10^6$	$\beta \times 10^7$ Calc.	$\beta \times 10^7$ Obs.
Heptane	8.66	1220[18]	1409	1340[19]
Acetone	11.22	1487[8]	1325	1176[9]
Carbon tetrachloride	11.47	1221[10]	1064	992[11]
		1236[13]	1078	1045[12]
Benzene	12.58	1248[14]	992	953[12]
		1237[15]	983	900[9]
Carbon disulfide	12.67	1218[13]	961	920[16]
		1190[10]	939	932[12]
Ethylene bromide	15.20	967[10]	636	604[9]
				600[17]
Bromoform	15.32	(939)[10]*	(613)	492[11]
		Calc. 754		
Ethylene chloride	14.17	1161[13]	819	785[11]
		1172[10]	827	

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[8] Zander. Lieb. Ann. **214,** 138 (1882).

[9] Richards and Shipeley, J. Am. Chem. Soc. **38,** 989 (1916).

[10] Thorpe. Proc. Roy. Soc. **24,** 283 (1876).

[11] Richards, Stull, Mathews and Speyers, J. Am. Chem. Soc. **34,** 971 (1912).

[12] Tyrer. J. Chem. Soc. **103,** 1675 (1913).

[13] Pierre, Ann. Chim. phys. [3] **33,** 199 (1851).

[14] Louguinine, Ann. Chim. phys. [9] **11,** 453 (1867).

[15] Kopp, Pogg. Ann. **72,** 1 (1847).

[16] Bridgman, Proc. Amer. Acad. **49,** 1 (1913).

[17] de Heen. Acad. Belg. (3) **9,** (1885).

[18] Bartoli and Stracciati, Atti Linc. (3) Mem. d. fis. **19,** 643, (1883–1884).

[19] Bartoli. Rend. Lomb. [2] 28 (1896).

* Impure, since melting point was 2.5° instead of 7.8°.