

684. *Pressure-Volume-Temperature Relations in Liquids and Liquid Mixtures. Part II.* The Compression Isotherms of Some Organic Liquids up to 1000 Atmospheres, and the Compressions of Some Aqueous and Non-aqueous Binary Liquid Mixtures.*

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The compression or fractional decrease in volume of eight chlorine-substituted hydrocarbons, and of acetone, has been measured at 25° and at pressures up to 1000 atmospheres. The relation of this quantity to other properties of the liquids is discussed.

The compression of a number of binary liquid mixtures at 25° and 1000 atmospheres has been measured over the whole composition range. Systems having water as one component show a compression minimum, which is related to other properties of these mixtures.

THE decrease in volume produced by a given pressure, at a constant temperature, varies considerably from liquid to liquid. Bridgman's measurements (see references in preceding paper) show that the compression, or fractional decrease in volume, $k = \Delta V/V_0$, of the least compressible non-metallic liquid, glycerol, is about 2.15×10^{-2} at 25° and 1000 kg./cm.², while for a light fluorocarbon oil, $k = 10.7 \times 10^{-2}$ under the same conditions (1 atm. = 1.0332 kg./cm.² = 1.0133 bars). The measurements now described, on eight chlorine-substituted hydrocarbons, were made to compare this variation of compression with differences in molecular structure in a related series of liquids. The pressure range employed corresponds with that over which Gibson and his co-workers (*J. Amer. Chem. Soc.*, 1938, **60**, 511, and subsequent papers) have made accurate compression measurements on a series of liquids, which include benzene derivatives. The results are comparable, as Gibson's values, presented in terms of bars, are readily converted into atmosphere units by means of the empirical Tait equation constants derived by him.

The electric contact method described in the previous paper is most accurate in a higher pressure range (as are Bridgman's piston-displacement and syphon methods) and was not used for these measurements.

EXPERIMENTAL.

The method used was that described by Adams (*J. Amer. Chem. Soc.*, 1931, **53**, 3769) and employed with slight modifications by Gibson (*loc. cit.*). The piezometer is of Pyrex glass and has the form shown in Fig. 1. The glass tube is closed at the top by a ground stopper having a mercury seal. From the base, a re-entrant capillary stem rises centrally inside the piezometer and is curled over at the end. The liquid to be compressed fills the piezometer, and, when pressure is applied, mercury is forced up the capillary, falls to the bottom, and remains trapped when the pressure is subsequently released. The external diameter of the piezometer is 1 cm., its overall length about 18 cm., and its internal capacity about 4 c.c. The capillary stem is about 5 cm. long and of 0.5 mm. internal diameter.

Before use the piezometer was carefully annealed (a procedure found essential by Adams and Gibson for reproducible results). Heating at 550° for 15 minutes was followed by cooling at the rate of 1°/min. for 20 minutes, and then as rapidly as the furnace would cool. The internal volume of the piezometer and of the capillary tube at 25° was determined by using mercury as filling liquid. The values accepted were the mean of several in close accordance.

The general lay-out of the high-pressure apparatus has already been described (*J.*, 1938, 784, Fig. 1). In this case, the thick-walled steel vessel ($\frac{3}{4}$ " inside diameter) is closed by a hard rubber "Poulter" packing held in place by a steel screw-plug. It is immersed in a thermostat bath stirred by a pump, and controlled to $\pm 0.1^\circ$. Pressure is conveyed from a hydraulic pump to an intensifier system and thence by a steel pipe-line to the bottom of the vessel. The pressure is shown by a Bourdon gauge on the low-pressure side of the intensifier, the effective ratio of which is about 9 : 1. It is not necessary in this case to know the exact value of this ratio because on the high-pressure side of the intensifier is connected a dead-weight pressure balance which measures directly the pressure in the vessel. The pressure balance is correct to at least ± 1 atm. at 1000 atm. The whole apparatus is filled with liquid paraffin, which is the pressure-transmitting medium.

Before a run, the piezometer was filled with the liquid under examination at a temperature below 25°, so that subsequent thermal expansion ensured that the tube was completely filled with liquid. Care was necessary to exclude very small bubbles, and it was found that silicone stop-cock grease was

* Part I, preceding paper.

a better lubricant than "Vaseline" for the stopper, as it was less readily attacked by the liquid during insertion. The filled piezometer was placed on a quantity of clean distilled mercury in a cylindrical steel holder, which was then immersed in liquid paraffin in the pressure vessel at thermostat temperature.

The hard rubber packing was pushed in very slowly by means of a brass screw-plunger. During this operation, the return valve to the pump was open so that no pressure could be generated in the vessel. Finally, the steel plug was screwed into position.

Pressure was applied to the vessel at 5-minute intervals in 100-atm. increments. This rate of increase proved slow enough to allow the heat of compression to be dissipated. The pressure was brought to within about 20 atm. of that desired in this way, and maintained at a steady value for 5–10 minutes to ensure temperature equalisation. The final adjustment of pressure was then made by slowly turning a screw-ram incorporated in the hydraulic pump.

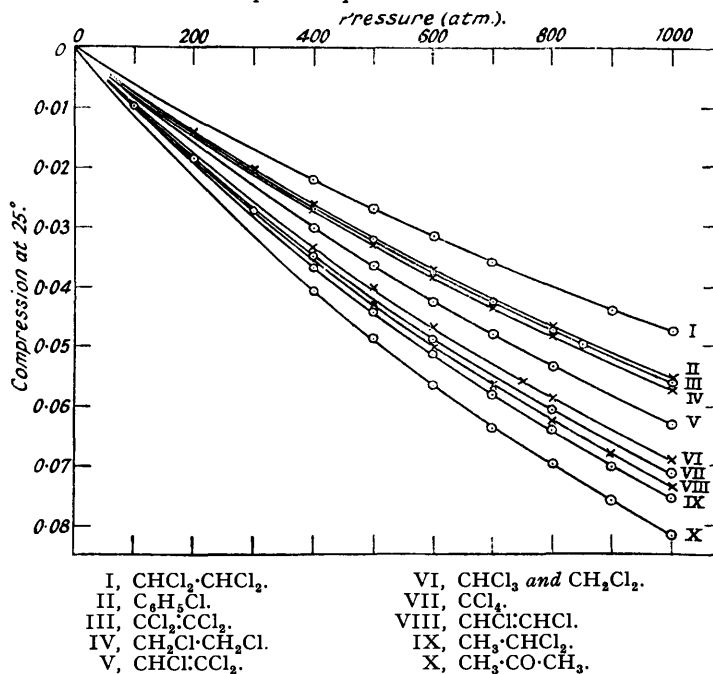
The release of pressure was also carried out at a slow uniform rate (occupying about 3 hours for a maximum pressure of 1000 atm.). The sequence of closing and opening valves by which the release

FIG. 1.
Pyrex-glass
piezometer in steel
container.



FIG. 2.

Compression-pressure isotherms.



was begun was so ordered that there was no possibility of an accidental increase of pressure, overshooting the desired maximum.

The mercury trapped in the piezometer was washed with alcohol and anhydrous ether, and weighed. The compression of the liquid is then given by

$$k = \frac{(V_{Hg})_0(1 - k_{Hg}) + (V_c)_0(1 - k_{Pyrex})}{V_0} + k_{Pyrex}$$

where k_{Hg} and k_{Pyrex} are the compressions of mercury and of the piezometer glass at 25° and the appropriate pressure; and V_0 , $(V_{Hg})_0$, and $(V_c)_0$ denote respectively the volume of liquid (total inside volume of tube and capillary), the volume of mercury trapped, and the inside volume of the capillary stem at 1 atm. and 25°. Values for k_{Pyrex} and k_{Hg} were taken from the results of Adams and Gibson (*J. Washington Acad. Sci.*, 1931, 21, 381) and Bridgman (*Proc. Amer. Acad. Arts Sci.*, 1912, 47, 432).

All the compressions at 1000 atm. for the pure liquids are the mean of several determinations which usually agreed to within 0.5%. Many of the other compressions were also measured more than once. Occasional check runs on redistilled water gave values about a mean $k = 3.96 \times 10^{-2}$ at 1000 atm. and 25°, which is satisfactorily close to the value 3.98×10^{-2} derived from Gibson and Loeffler's work (*J. Amer. Chem. Soc.*, 1941, 63, 898). The accuracy of the measurements at 1000 atm. is thus estimated to be better than $\pm 1\%$.

The compressions of the mixtures were determined with the same accuracy, although usually only one measurement was made at any particular composition.

Materials.—Acetone (two separate samples) and chloroform were obtained in "AnalaR" quality and were used after being once fractionated in an all-glass Widmer column. The boiling ranges were 56.0–56.3° and 61.0–61.3° and the refractive indices (n_D^{20}) 1.3590 and 1.4465, respectively. The other liquids were dried (CaCl_2) (in some cases a preliminary shaking with dilute potassium hydroxide solution being necessary), and fractionated twice, as above. Boiling ranges were: methylene dichloride 40.0–40.2°; *trans*-dichloroethylene 48.0–48.5°; ethylidene chloride 57.3°; 1:2-dichloroethane 83.5–83.7°; trichloroethylene 87.0–87.5°; tetrachloroethylene 121.0–122.0°, and tetrachloroethane 146.0–146.5°. Refractive indices (n_D^{20}) were measured with an Abbé refractometer and agreed to within 0.0005 with values given in the International Critical Tables.

DISCUSSION.

A. Compression Isotherms of Single Liquids.—The compressions of the eight chlorine-substituted hydrocarbons, and of acetone, are given in Table I. The values for carbon tetrachloride and chlorobenzene which are also included have been obtained from the results of Gibson and Loeffler (*loc. cit.*; *J. Amer. Chem. Soc.*, 1939, 61, 2515) by conversion to atmosphere pressure units. The compression curves are shown in Fig. 2.

TABLE I.
Percentage decrease in volume of liquids under pressure.

Compounds	p (atm.) =	Compression $k \times 10^2$ at 25°.								
		400	500	600	700	750	800	850	900	1000
$\text{CHCl}_3 \cdot \text{CHCl}_2$	2.20	2.68	3.15	3.60	—	—	—	—	4.41	4.78
$\text{C}_6\text{H}_5\text{Cl}$ *	2.63	—	3.71	—	—	4.69	—	—	—	5.56
$\text{CCl}_2 \cdot \text{CCl}_2$	2.64	3.19	3.74	4.26	—	4.73	4.97	—	—	5.63
$\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$	2.70	3.28	3.84	4.34	—	4.84	—	—	—	5.76
$\text{CHCl} \cdot \text{CCl}_2$	3.02	3.64	4.25	4.80	—	5.36	—	—	—	6.32 _s
CH_2Cl_2	3.30	4.01	—	5.27	—	5.88	—	—	—	6.93
CHCl_3	3.35	4.01	4.69	—	5.59	5.89	—	—	—	6.93
CCl_4 *	3.53	—	4.90	—	—	6.09	—	—	—	7.15
$\text{CHCl} \cdot \text{CHCl}$ †	3.58	4.30	5.02	5.66	—	6.26	—	—	6.80	7.38
$\text{CH}_3 \cdot \text{CHCl}_2$	3.69	4.43	5.15	5.82	—	6.41	—	—	7.03	7.56
$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$	4.07	4.87	5.66	6.38	—	6.96	—	—	7.59	8.18

* Gibson and Loeffler.

† *trans*- $\text{CHCl} \cdot \text{CHCl}$, b. p. 48.4°.

In the series of chloro-compounds, no simple correlation has been found between any aspect of the molecular structure and the sequence of the compression isotherms. Bridgman (*Proc. Amer. Acad. Arts Sci.*, 1949, 77, 129) has measured the rough compressions up to 40,000 kg./cm.², at room temperature, of 30 hydrocarbons and also finds no correlation between the compressions and structural factors, such as the C:H ratio in the molecule, the type of the carbon-carbon bonds, and the type (whether straight-chain, single ring, or double ring) of the molecule. The reason is presumably that the shape and intensity of the molecular force field in the liquid is related in a complex way to the molecular structure. In the liquids of Table I, three kinds of intermolecular force are probably operative, *viz.*, the cohesive van der Waals forces opposing the thermal movement of the molecules, shorter-range intermolecular repulsions, and, in most cases, long-range dipole-dipole interaction. A change in molecular structure may, in general, be expected to affect these components in divergent ways.

The benzene derivative and the two liquids containing four chlorine atoms in the molecule are likely to be the most polarisable, and so to have the strongest cohesive forces, and these three are the least compressible of the liquids. Similarly, Bridgman (*ibid.*, 1933, 68, 1) has shown that the compressions of alkyl halides, when the alkyl group is unchanged, decrease in the order $\text{Cl} > \text{Br} > \text{I}$.

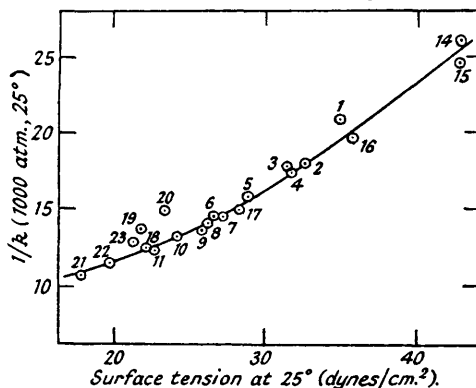
Compression and Surface Tension.—A relation has been sought between the compression and some property of the liquids at normal pressure. There are indications of an approximate interdependence between the compression at a given pressure and the free energy of vaporisation. Unfortunately, there are too few experimental values of this quantity, at 25°, for an adequate comparison. There exists, however, an approximate relation between compression and surface tension which is shown in Fig. 3. In this figure, the reciprocal of the compression at 1000 atm. and 25° is plotted against the surface tension at the same temperature. The numbers of the points 1–11 refer to the liquids in Table I, reading downwards. The rest are shown in Table II and refer to liquids for which k at 1000 atm. and 25° is known with comparable or better accuracy. Water and ethylene glycol cannot conveniently be shown on

TABLE II.
Percentage decrease in volume at 1000 atm.

Liquid	$k \times 10^3$ at 25° and 1000 atm.	Reference	Liquid	$k \times 10^3$ at 25° and 1000 atm.	Reference
12. Ethylene glycol	3.16	Gibson and Loeffler (<i>loc. cit.</i>)	18. Methanol	8.09	Gibson (see below)
13. Water	3.98		19. Ethanol	7.30	This paper
14. Aniline	3.83		20. Propanol	6.75	This paper
15. Nitrobenzene	4.06		21. Hexane	9.45	Part I (preceding paper)
16. Bromobenzene	5.09		22. Heptane	8.74	
17. Benzene	6.70		23. Octane	7.79	

Fig. 3, and are in any case probably affected by hydrogen-bonding. It appears justifiable to use arbitrarily the compressions at 1000 atm., as the isotherms are all of the same form and probably do not cross before the freezing pressures are reached. The general conclusion from Fig. 3 is that the greater the net intermolecular attractive forces at ordinary pressure, the smaller is the compression at high pressures. The relationship shown is obviously inexact but is sufficient for a rough estimate of the compression of a liquid from the surface tension. At much higher pressures it may tend to break down because the intermolecular repulsive forces become far larger than they are in liquids at ordinary pressure. Bridgman (1949, *loc.*

FIG. 3.
Relation between compression and surface tension.



cit.) has shown, however, that the initial sequence of the hydrocarbon isotherms persists up to 40,000 kg./cm.², even though the volume decrements in the 20,000—40,000 interval are irregular.

Tait's Equation and Hudleston's Relation.—The isotherms of Fig. 1 may be represented by Tait's equation

$$k = C \log (B + P)/(B + P_0)$$

where B and C are constants and P_0 is atmospheric pressure (see discussion in Part I). The values of B and C at 25° obtained from the data are shown in Table III. The data for the

TABLE III.
Constants of Tait's equation.

Liquid	C	B , atm.	Liquid	C	B , atm.
CHCl ₂ -CHCl ₂	0.2156	1498	CHCl ₃ and CH ₂ Cl ₂	0.2391	1052
C ₆ H ₅ Cl	0.2103	1191	CCl ₄	0.2126	853.9
CCl ₂ -CCl ₂	0.2215	1255	CHCl:CHCl	0.2518	1036
CH ₂ Cl-CH ₂ Cl	0.2233	1231	CH ₃ -CHCl ₂	0.2296	879.3
CHCl:CCl ₂	0.2425	1213	CH ₃ -CO-CH ₃	0.2356	815.0

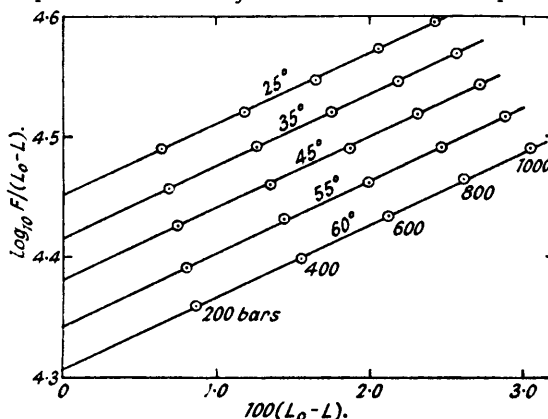
liquids also fit the straight-line plot required by a relation derived by Hudleston (*Trans. Faraday Soc.*, 1937, **33**, 97) from consideration of a simple exponential law of intermolecular force. According to this, the function, $\log F/(L_0 - L)$, should vary linearly with $L_0 - L$, where L_0 and L are the length of side of a cube containing a given mass of liquid at unit pressure

and at pressure P , respectively, and where $F = L^2P$. This rule is apparently of very wide validity and holds over a large pressure range. Fig. 4 shows the lines for carbon tetrachloride (Gibson's data) at different temperatures. Bridgman's combined data on *n*-propyl alcohol at 50° up to 50,000 kg./cm.² (*Proc. Amer. Acad. Arts Sci.*, 1913, 49, 3; *J. Chem. Physics*, 1945, 9, 794) give a straight line over most of the range; a divergence above 35,000 atm. could be entirely attributed to a 2% error in the volume decrements. When the slopes of the lines for different liquids (each for a mass of 1 g.-mol.) are compared they are found to vary by only a few units %, and for benzene and carbon tetrachloride (Gibson) the slopes are independent of temperature.

Hudleston stated that water and acetone are exceptions, but the apparent discrepancy seems due to small experimental irregularities in Bridgman's data at the lower end of his pressure range. Adams's results (*loc. cit.*) for water at 25° up to 12,000 bars give a good straight line, and the data for acetone in Table I (obtained for the purpose of this comparison) give a straight line in the region below 2000 atm. in which Bridgman's results (*loc. cit.*, 1913) are

FIG. 4.

Compression data for CCl_4 (Gibson and Loeffler) plotted according to Hudleston's equation. (The points are calculated for unit volume at each temperature.)



divergent. The value for acetone at 1000 atm. is the mean of seven determinations on two samples, which all agreed to within $\pm 0.6\%$. The piston-displacement method only develops its maximum accuracy at higher pressures, and Gibson has shown (*J. Amer. Chem. Soc.*, 1935,

TABLE IV.

Compression of mixtures at 1000 atm.

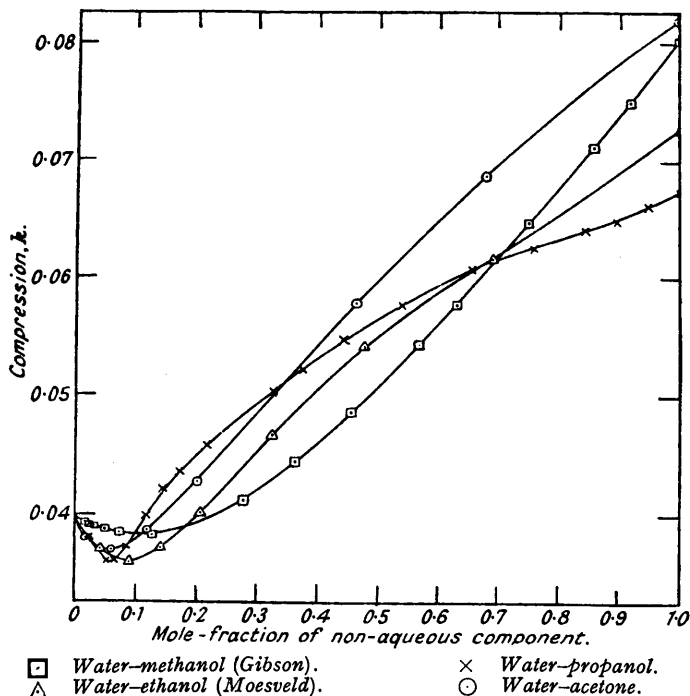
(W and n refer to the first-named component in the mixture.)

W , wt. %	n	100k	W , wt. %	n	100k	W , wt. %	n	100k
Acetone-Water.								
0	0	3.96	29.71	0.1160	3.87 ₅	87.16	0.6780	6.83
5.32	0.0172	3.79	44.86	0.2016	4.27	100.00	1.0000	8.18
16.69	0.0585	3.69	73.30	0.4601	5.77			
Propanol-Water.								
6.44	0.0202	3.80	40.65	0.1703	4.33	86.25	0.6529	6.05
15.79	0.0533	3.60	48.03	0.2186	4.57	91.24	0.7577	6.24
17.90	0.0613	3.62	61.81	0.3270	5.01	94.65	0.8411	6.42
23.55	0.0845	3.71	66.70	0.3754	5.20	96.56	0.8945	6.47
30.29	0.1153	3.98	72.46	0.4412	5.47	98.40	0.9488	6.62
35.46	0.1415	4.21	79.66	0.5404	5.76	100.00	1.0000	6.75
Acetone-Chloroform.								
0	0	6.93	39.42	0.5724	7.65	78.73	0.8818	8.08
4.87	0.0950	7.02	53.10	0.6993	7.85	100.00	1.0000	8.18
22.55	0.3745	7.37	69.25	0.8220	8.02			
Ethanol-Propanol.								
0	0	6.75	43.71	0.5034	7.02	100.00	1.0000	7.30
11.12	0.1405	6.79	89.91	0.9208	7.27			

57, 1551) that methanol also undergoes a greater compression at 1000 bars than Bridgman's values indicate. Hudleston's equation is thus a useful check on experimental results, but its theoretical basis remains obscure and its application is limited by the fact that it cannot be transformed into a simple expression for volume as a function of pressure.

B. *Compressions of Binary Liquid Mixtures*—The object of these measurements, at 25° and 1000 atm., was to find whether the compressions of the mixtures can be calculated additively from those of the pure components, or whether there are major departures from the straight-line compression-composition graph which this implies. Data already available include results for the methanol-water and acetic acid-water systems at 25° and 1000 bars (Gibson, 1935, *loc. cit.*, and *ibid.*, p. 284), ethanol-water at 25° and 500, 1000, and 1500 atm. (Moesveld, *Z. physikal. Chem.*, 1923, **105**, 450), the extensive measurements on aniline-nitrobenzene, aniline-benzene, and aniline-chlorobenzene mixtures by Gibson and Loeffler (*loc. cit.*, 1939; *J. Physical Chem.*, 1939, **43**, 207), and the values for hydrocarbon mixtures in Part I

FIG. 5.
Compression of aqueous binary mixtures at 1000 atm., 25°.



of this series. Dolezalek and Speidel (*Z. physikal. Chem.*, 1920, **94**, 72) have measured the compressibilities, $\beta = -(\partial V/\partial P)_T/V$, of benzene-carbon tetrachloride, benzene-ethylene dichloride, and chloroform-ether mixtures at pressures from 30 to 600 kg./cm.², but these results are not in a form in which they can be compared with the others. Richards and Chadwell (*J. Amer. Chem. Soc.*, 1925, **47**, 2283) have examined the depression in the compressibility of water produced by ether, ethanol, urethan, and methyl acetate at low concentrations, and have measured average compressibilities in the range 100–300 bars.

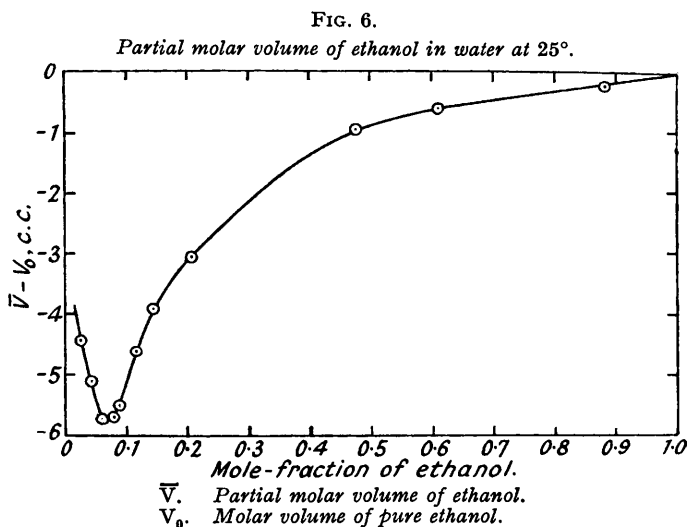
The results now presented are for the mixtures acetone-water, propanol-water, ethanol-propanol, and acetone-chloroform, and are given in Table IV, where n is the mole-fraction and k the compression at 25° and 1000 atm. The greatest departure from additivity so far found in non-aqueous mixtures occurs in the aniline-benzene system (Gibson and Loeffler) which has a lower compression than would be expected from the values for the pure components. The maximum divergence at 25° and 1000 bars amounts to about 5%. The compressions of aniline-nitrobenzene mixtures are up to 1% greater than additive under the same conditions. Both ethanol-propanol and acetone-chloroform (Table IV) give a linear compression-composition relation within the experimental error. Strong interaction occurs in the last-named

system, but presumably after the molecular complexes have been formed the "intermolecular" forces are similar to those in the pure liquids, as far as compression is concerned.

The compressions for the two aqueous mixtures, and the previous data of Gibson and of Moesveld for methanol-water and ethanol-water, are shown in Fig. 5. All the curves pass through a minimum at low concentrations of the non-aqueous component, the sharpness and position of the minimum varying from mixture to mixture. Also in the middle of the composition range the compression of the propanol-water mixtures is 3-4% above that to be expected additively.

The existence of the compression minima may be correlated with other properties of these mixtures. At similar concentrations there occur maxima in the velocity of ultrasonic waves in the mixtures (Burton, *J. Acoust. Soc. Amer.*, 1948, **20**, 186), and so presumably minima of adiabatic compressibility. Table V compares the compositions at which compression minima occur with those corresponding to the velocity maxima as estimated from Burton's curves.

Also tabulated are the maxima in the heats of mixing derived from Bose's results (*Z. physikal. Chem.*, 1907, **58**, 585), and two values for minimum partial molar volumes (calculated



from the specific volumes given by International Critical Tables), which also appear to be related to the compression minima. Fig. 6 shows the minimum in the partial molar volume of ethanol in ethanol-water mixtures at 25°. The minimum for methanol is rather broader and less pronounced.

TABLE V.

Compositions at which maxima or minima in various properties occur.

	Mol.-fractions of non-aqueous component.			
	Methanol.	Ethanol.	Propanol.	Acetone.
Compression minimum (at 25°; 1000 bars or atm.)	0.125	0.09	0.06	0.06
Ultrasonic velocity maximum (at 25° or 27°)	0.18	0.11	0.05	0.07
Maximum heat of mixing at 25°	~0.25	~0.15	~0.08	—
Minimum partial molar volume at 25°	0.12	0.07	—	—

As would be expected from the findings for pure liquids, it seems evident that the compression minima at 1000 atm. occur in a concentration region in which the cohesive internal forces in the mixtures are strongest.

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