683. *Pressure–Volume–Temperature Relations in Liquids and Liquid Mixtures. Part I. The Compression of* n-*Hexane,* n-*Heptane,* n-*Octane, and of their Binary and Ternary Mixtures, up to* 5000 *Atmospheres.*

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The compression of *n*-hexane, *n*-heptane, *n*-octane, and of binary and ternary mixtures of these hydrocarbons has been determined up to 5000 atmospheres, and at 0°, 25°, 40°, and 60°. The isotherms are expressed in the form of the Tait equation.

The energy–volume coefficients, $(\partial E/\partial V)_T$ and the pressure coefficients, $(\partial P/\partial T)_V$, are found to be pure volume functions, and at all the temperatures and pressures employed the hydrocarbons mix without expansion or contraction in volume.

Measurements of the decrease in volume undergone by liquids at high pressures are an important source of information about the intermolecular forces, and contribute towards a general theory of the liquid state. The first systematic study was made by Amagat (*Ann. Chim. Phys.*, 1893, **29**, 68, 505) on twelve organic liquids up to 3000 atmospheres and in the range 0—200°. Bridgman (" The Physics of High Pressure," 2nd edn., 1949) developed new experimental methods by which Amagat's results were repeated and extended to 12,000 kg./cm.^{2}, between 20° and 80°. Bridgman (*op. cit.*; see also *Proc. Amer. Acad. Arts Sci.*, 1949, **77**, 115—146) has measured the volume decrements of a large number of other liquids to 12,000 kg./cm.^{2}, and in many cases to 40,000 or 50,000 kg./cm.^{2}, but generally not at a sufficient number of different temperatures to enable detailed thermodynamic analysis of his results to be made.

Gibson and his co-workers (*J. Physical Chem.*, 1939, **43**, 207; *J. Amer. Chem. Soc.*, 1938, **60**, 511, and subsequent papers to 1941) have obtained accurate data for eight liquids and some liquid mixtures, at pressures up to 1000 bars. These authors have consistently used the Tait equation to represent their pressure–volume isotherms, and have calculated various functions, such as the energy–volume coefficient and the pressure coefficient for the liquids. The general use of three different units of pressure (1 normal atmosphere = 1·0133 bars = 1·0322 kg./cm.^{2}) is an obstacle to the exact comparison of results from different laboratories, but this may be done from the pressure–volume curves, or by calculation where the Tait constants have been evaluated.

This paper presents the results of volume measurements on *n*-hexane, *n*-heptane, *n*-octane, and mixtures of these hydrocarbons, up to 5000 atmospheres, which was the maximum pressure with the apparatus available, and at 0°, 25°, 40°, and 60°.

Experimental.

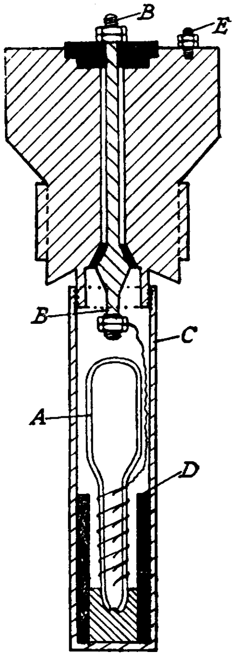
The general arrangement of the high-pressure apparatus has been described previously (see *J.*, 1938, 784, Fig. 1). The pressure vessel is a thick-walled steel cylinder, closed at the top by a steel screw plug seating on a lens ring, and immersed in a thermostat bath. Pressure is generated by a hand pump and transmitted through an intensifier to the bottom of the vessel along a steel pipe-line.

The liquid hydrocarbon is contained in a glass tube, *A*, of the form shown in Fig. 1. The tubes used were of Jena Red Line or Pyrex glass and were carefully annealed. The bulb is of approximately 8 mm. internal diameter, and the ratio of the volume of the bulb to that of the stem is about 4 : 1. A series of contacts of fine platinum wire (diameter 0·005 inch) are sealed into the tube, so that their ends lie along the central axis and point downwards to make clean and sharp contact with the mercury. A length of silk-covered constantan resistance wire (20 ohms per yard) is soldered to the lowest platinum contact and wound spirally round the tube, the other contacts being soldered to bared sections. The upper end of the resistance wire is attached to the lower end of a steel electrode, *B*, which is insulated from the screw plug and passes upward through it to an insulted terminal on its upper face. A cylindrical steel holder, *C*, screws on to the base of the plug and surrounds the glass tube. The holder contains mercury which seals the open end of the stem. Holes in the wall of the holder ensure pressure equalisation inside and out, and the thin-walled ebonite cylinder, *D*, prevents the contacts from accidentally touching the holder walls. Externally the electrical circuit is made from the electrode terminal through a milliammeter and two-volt accumulator to the screw plug at *E*, and thus to the mercury in the holder. When the plug has been tightened into position in the vessel, the glass tube and the mercury holder are immersed in the pressure transmitting fluid—an 80% paraffin oil–20% liquid paraffin mixture. With increasing pressure the mercury rises in the stem, successively cutting out parts of the resistance of the constantan wire and causing abrupt increases in the milliammeter reading.

Preliminary experiments, using a tube open at both ends, established that with rising and falling mercury columns the contacts were made sharply and reproducibly, and did not depend on the nature of the liquid above the mercury. The glass tubes were calibrated by weighing when empty, when full of mercury, and when containing sufficient mercury just to touch each contact in turn. In use the tubes were frequently recalibrated, satisfactory agreement being obtained.

A weighed tube (containing a globule of mercury to seal the bottom of the stem on inversion, and during transfer to the mercury holder) was filled with liquid, inverted quickly, stood in a mercury-containing crucible of known weight, and reweighed after any overflow liquid had evaporated. After a little practice, this operation could be performed without introducing air bubbles, and with the minimum of overflow. The tube was transferred to the steel mercury holder, which was attached to the plug and screwed into position in the pressure vessel. The thermostat bath was then heated or cooled, about 5 hours being allowed for the apparatus to attain a steady temperature, which was controlled to ±0·1°. If the bath was heated, a pressure of about 500 atm. was first applied to prevent liquid from expanding out of the glass tube.

FIG. 1.



The rate of increase of pressure was controlled to allow time for the heat of compression to dissipate. Pressure was increased between contact points by about 500 atm. every 10 minutes. When the new contact was made, pressure was released until the contact was just broken, and ½ hour was allowed for the temperature to become steady. The contact was then remade by creating extra pressure in the pump and opening the valve to the intensifier very slowly. Two, and often three, runs were carried out to establish each isotherm.

Calculation of Results and the Experimental Error.—The compression or fractional decrease in volume $k = \Delta V/V_0$, where V_0 is the initial volume, was calculated from the density of the liquid and from the known volume of the tube at each contact as determined by the calibration. The tube volumes were corrected for temperature change by using the following coefficients of cubic expansion: Jena glass $0{\cdot}2533 \times 10^{-4}$; Pyrex $0{\cdot}108 \times 10^{-4}$. The correction for the compression of the glass of the tube was made by subtracting the compression of the glass from the calculated compression of the liquid. The appropriate values are: $k_{\text{Jena}} \times 10^6 = 2{\cdot}206 + 0{\cdot}0028t$ per atm.; $k_{\text{Pyrex}} \times 10^6 = 3{\cdot}00$ per atm., as determined by Perman and Urry (*Proc. Roy. Soc.*, 1928, **40**, 186) and Adams and Gibson (*J. Washington Acad. Sci.*, 1931, **21**, 381).

Repeated recalibrations were performed, and in one test a calibrated tube was placed under 5000 atm. pressure for 5 hours. In no case were the variations found sufficient to affect the final volumes recorded in Table II by more than 0·02%. The possible error in the weighings could produce a variation of ±0·01% in the final volumes.

The Bourdon gauge, on the low-pressure side of the intensifier, was calibrated against a pressure balance accurate to 1 atm., and could be read to ±1 atm. The intensifier ratio (approx. 5 : 1) is not as large as that calculated from the ratio of the cross-sectional areas of the two pistons comprising the intensifier, and it was found to vary with the pressure used, presumably because of the changing areas of contact between the pistons and the cylinder walls. The ratio was determined over the whole pressure range and found to alter appreciably at the lower pressures but to become constant above 300 atm. (low-pressure side).

From these considerations it appears that the maximum accuracy is attained at pressures above 1000 atm. and that the volumes determined in this range are accurate to within about ±0·04%.

Materials.—*n*-Heptane and *n*-octane were synthetic products obtained from the Eastman-Kodak Co.; *n*-hexane was supplied by the Anglo-Iranian Oil Co. The hydrocarbons were shaken with concentrated sulphuric acid, washed with distilled water, and refluxed over calcium turnings. They were then fractionated, a middle fraction boiling over a temperature range not exceeding 0·15° being collected. Samples were de-aerated in an all-glass apparatus before use. The boiling ranges and refractive indices were as follows: *n*-hexane 68·8—68·85°, n_D^{20} 1·3750; *n*-heptane 98·4—98·5°, n_D^{25} 1·3844; *n*-octane 125·4—125·55°, n_D^{20} 1·3975.

For the calculations, it was necessary to know the densities of the liquids and mixtures at the temperatures employed. There was not sufficient material to allow determination of density–composition curves at all four temperatures, so the following procedure was used. The densities of the pure liquids at 25° and 40° were accurately determined in a specific gravity bottle and found to be in excellent agreement with those given in International Critical Tables. The densities of two mixtures of each of the three pairs of liquids were also determined at these two temperatures and it was found that the liquids mixed without change in volume. It was therefore considered justifiable to use the density–temperature equation given in I.C.T. to calculate the densities of the liquids at the other two temperatures, and to compute the densities of the mixtures additively. In Table I are given the constants of the specific volume–temperature equation for the pure hydrocarbons expressed in the form:

$$V = V_0 + \alpha t + \beta t^2 + \gamma t^3$$

where V_0 s the specific volume at 0°.

The composition of the mixtures at 25° was checked against a refractive index–composition curve for the sodium *D* line, determined with an Abbé refractometer. A straight-line relationship was found, the heptane–octane mixtures, for example, being represented by the equation $n_D^{25} = 1{\cdot}072 \times 10^{-4}w + 1{\cdot}3844$, where w is the weight % of *n*-octane in the mixture. In no case was there a significant change in the composition of a mixture during the experiments.

TABLE I.

Thermal expansion coefficients.

	V_0.	$\alpha \times 10^3$.	$\beta \times 10^6$.	$\gamma \times 10^8$.
n-Hexane	1·4770	1·851	4·714	0·9524
n-Heptane	1·4275	1·717	2·102	1·024
n-Octane	1·3918	1·599	0·817	1·309

TABLE II.

Relative volumes.

Press.	Volume				Press.	Volume			
(atm.)	0°	25°	40°	60°	(atm.)	0°	25°	40°	60°
				n-Hexane.					
1	1·0000	1·0334	1·0556	1·0881	3000	0·8446	0·8561	0·8636	0·8741
500	0·9501	0·9729	0·9876	1·0085	3500	0·8327	0·8434	0·8503	0·8600
1000	0·9175	0·9357	0·9475	0·9642	4000	0·8221	0·8319	0·8386	0·8477
1500	0·8934	0·9089	0·9190	0·9333	4500	0·8126	0·8219	0·8280	0·8369
2000	0·8742	0·8880	0·8969	0·9095	5000	0·8040	0·8128	0·8186	0·8268
2500	0·8582	0·8707	0·8788	0·8903					
		n-Heptane.					*n*-Octane.		
1	1·0000	1·0311	1·0509	1·0790	1	1·0000	1·0289	1·0475	1·0731
500	0·9538	0·9760	0·9896	1·0085	500	0·9596	0·9807	0·9942	1·0119
1000	0·9229	0·9409	0·9520	0·9672	1000	0·9313	0·9487	0·9596	0·9739
1500	0·8996	0·9153	0·9249	0·9379	1500	0·9096	0·9247	0·9342	0·9465
2000	0·8811	0·8949	0·9035	0·9151	2000	0·8919	0·9053	0·9138	0·9248
2500	0·8654	0·8782	0·8860	0·8965	2500	0·8771	0·8993	0·8971	0·9069
3000	0·8521	0·8639	0·8711	0·8809	3000	0·8642 *	0·8755	0·8827	0·8919
3500	0·8404	0·8514	0·8582	0·8673	3500	—	0·8635	0·8702	0·8788
4000	0·8301	0·8403	0·8467	0·8553	4000	—	0·8528	0·8591	0·8672
4500	0·8206	0·8304	0·8364	0·8445	4500	—	0·8431	0·8489	0·8567
5000	0·8121	0·8214	0·8272	0·8348	5000	—	0·8342	0·8399	0·8472

* Freezes above this pressure.

TABLE III.

Constants of Tait's equation.

For all liquids and mixtures at all temperatures, $C = 0{\cdot}2172$.

	B (atm.)			
Liquid	0°	25°	40°	60°
n-Hexane	713·9	579·1	508·6	424·5
n-Heptane	788·6	653·1	582·9	498·8
n-Octane	931·4	776·5	696·8	599·1
C_7–C_8 Mixtures :				
22·04% C_8	816·4	678·2	605·2	518·8
41·32% ,,	841·8	700·7	625·1	537·4
65·37% ,,	876·1	731·6	653·7	561·8
82·73% ,,	902·4	752·8	674·5	581·0
C_7–C_6 Mixtures :				
31·93% C_7	736·9	602·0	531·5	446·8
65·73% ,,	762·2	626·8	556·3	471·7
C_6–C_8 Mixtures :				
33·82% C_8	778·7	638·2	564·7	476·1
61·48% ,,	837·9	692·6	615·8	523·9
Ternary mixtures :				
35·26% C_6; 31·72% C_7; 33·02% C_8	803·1	662·5	588·5	500·1
19·11% C_6; 41·16% C_7; 40·73% C_8	810·4	670·9	597·4	509·5

(All compositions are given as weight percentages.)

Results.—The experimental points were plotted and, from the smooth pressure–volume isotherms drawn through them, volumes were read off at intervals of 500 atm. pressure. These values for the pure liquids are shown in Table II. The results for the pure hydrocarbon at 0° correspond well with those of Bridgman (*Proc. Amer. Acad. Arts Sci.*, 1931, **66**, 185), who uses kg./cm.^{2} as his pressure unit.

All the P–V–T data may be expressed accurately by the Tait equation (see p. 3089), *viz.*,

$$\Delta V/V_0 = k = C \log (B + P)/(B + P_0)$$

where B and C are constants and k is the compression, or fractional change in volume, when the pressure changes from P_0 to P. Table III gives the values of B for the pure liquids and their mixtures at the four temperatures. The constant $C = 0{\cdot}2172$ and is found to be the same for all the liquids and their mixtures and to be independent of temperature. (*N.B.* Gibson's usage has been followed in giving the value of C. If the Tait equation is expressed in terms of natural logarithms, $0{\cdot}4343C$ must replace the above figure).

DISCUSSION.

1. *Tait's Equation.*—This equation was found by Tait (1888) to fit the compression data for water. Wohl (*Z. physikal. Chem.*, 1921, **99**, 234) and Carl (*ibid.*, 1922, **101**, 238) found that it satisfactorily represented Amagat's (*loc. cit.*) and Bridgman's data (*Proc. Amer. Acad.*, 1913, **49**, 1), and noted the temperature-independence of C. Gibson and his associates (*loc. cit.*; see also *J. Amer. Chem. Soc.*, 1934, **56**, 4; 1935, **57**, 284) have made a thorough study of the equation and find that it closely fits Adams's data (*ibid.*, 1931, **53**, 3769) on water up to 10,000 bars at 25°, and Bridgman's results (*Proc. Amer. Acad. Arts Sci.*, 1931, **66**, 185; 1932, **67**, 1; 1933, **68**, 1) on numerous non-volatile liquids at different temperatures over the same range. Gibson finds that C has the same value ($= 0{\cdot}21591$) for benzene, chlorobenzene, bromobenzene, aniline, and nitrobenzene; and for aniline–nitrobenzene, aniline–benzene, and aniline–chlorobenzene mixtures—an example which parallels the constancy of C for the hydrocarbons and hydrocarbon mixtures described in this paper.

The theoretical basis of Tait's equation is still very obscure. The temperature-independence of C, and the fact that it varies little from liquid to liquid, have led to the supposition that it depends on the repulsive forces between the molecules.

Gibson and Kincaid (1938, *loc. cit.*) have tentatively identified $B + P$ with the difference between the expansive thermal or kinetic contribution to the pressure and the internal attractive pressure. They write $P = T.\,\mathrm{f}(V) + \phi(V) + \psi(T)$, in which $T.\,\mathrm{f}(V)$ is the kinetic contribution to the pressure, $\phi(V)$ is the purely volume-dependent part of the internal pressure, arising from the attractive forces, and $\psi(T)$ is the temperature-dependent difference between the attractive pressure and the kinetic repulsion which is regarded as equal to B. $\psi(T)$ is generally a cohesion in liquids and is balanced by the intermolecular repulsions. B decreases with increasing temperature and on this interpretation must change sign at the critical temperature.

For the liquids that Gibson investigated $(\partial P/\partial T)_V$ was found to be not a pure function of volume but to vary slightly with temperature. This appears to indicate interaction between the component terms of P in the above equation. It is thus doubtful whether precise physical significance can be attached to these terms, and hence to B or $B + P$, for liquids in which $(\partial P/\partial T)_V$ is not a pure volume function. In our experimental range, as discussed below, this coefficient is temperature-invariant and Gibson's view may hold more exactly.

The ability of Tait's equation to represent the P–V isothermals adequately has been demonstrated by Gibson through a comparison of values of the compressibility, $(\partial V/\partial P)_T/V$, at 1 atm., obtained experimentally, with those calculated from Tait's equations for his liquids. The agreement was always to within 1%. Such a comparison is possible for heptane and octane, by using the adiabatic compressibilities measured by Freyer, Hubbard, and Andrews (*J. Amer. Chem. Soc.*, 1929, **51**, 759). The relation given in their paper was used to calculate the isothermal compressibilities, values for the specific heats being taken from Parks, Huffman, and Thomas (*ibid.*, 1930, **52**, 1033). The satisfactory agreement found is shown in Table IV.

TABLE IV.

Isothermal compressibilities at 1 *atmosphere* ($\times$ 10^6).

Liquid	0°	25°	40°	60°	Source
n-Heptane	119·5	144·2	161·5	188·7	Tait's equation
,,	121·4	146·0	163·7	190·1	F, H, and A
n-Octane	101·2	121·3	135·2	157·2	Tait's equation
,,	103·7	123·2	138·4	159·3	F, H, and A

At the same time it was found that values of the dilatation $(\partial V/\partial T)_{P=0}$ calculated from the compressibility and the pressure coefficient by the reaction

$$\left(\frac{\partial V}{\partial T}\right)_{P=0} = \left(\frac{\partial V}{\partial P}\right)_T \times \left(\frac{\partial P}{\partial T}\right)_V,$$

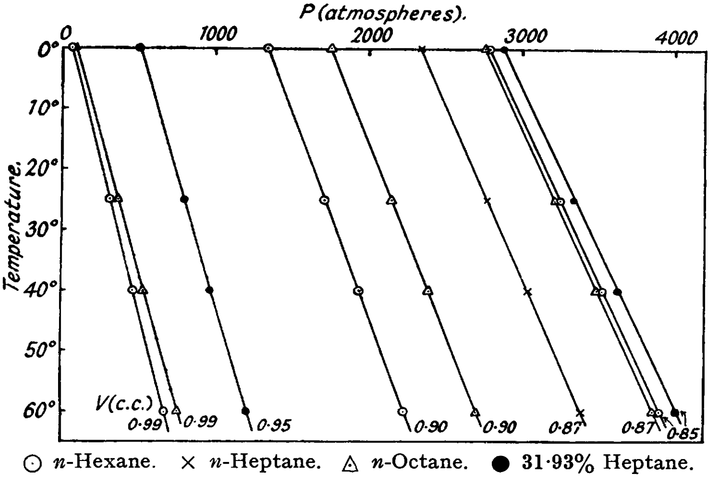
agreed satisfactorily with those obtained from specific-volume measurements for all three hydrocarbons.

2. *The Pressure Coefficient* $(\partial P/\partial T)_V$.—For all the liquids and their mixtures, the isochores are straight lines, within the experimental error, as shown by the examples in Fig. 2. The pressure coefficients, $(\partial P/\partial T)_V$, are thus pure volume functions within the range investigated. The coefficients decrease with increasing volume at constant temperature.

There is a conflict of evidence as to whether or not the pressure coefficient for liquids is in general a pure volume function. Gibson found a small but definite degree of temperature-dependence at constant volume for all the liquids that he measured. Among these were ethylene glycol and highly polar monosubstituted benzenes, but they also included benzene itself and carbon tetrachloride. Bridgman (1913, *loc. cit.*) also finds a temperature variation in a series of polar liquids and presents detailed calculations for the case of carbon disulphide. Hildebrand (*Physical Rev.*, 1929, **34**, 984) attributes the variations found by Bridgman to experimental irregularites, at least in the case of ether (the most symmetric and least polar liquid studied), and gives an interesting discussion of intermolecular forces in this substance. Subsequently, Bridgman (1931, *loc. cit.*) presented new data which also indicate a variation of the pressure coefficient at constant volume, and advanced general reasons (*Rev. Mod. Physics*, 1935, **7**, 1), based on molecular deformability, for supposing that this is normally to be expected. These data include results for normal hydrocarbons up to 10,000 kg./cm.^{2}, but only three isotherms (at 0°, 50°, and 95°) were determined, and a small error in one of these would invalidate his conclusions. A variation would perhaps be more apparent over Bridgman's greater pressure range, but within the limits of the present measurements the coefficients for *n*-hexane, *n*-heptane, and *n*-octane are sensibly constant at constant volume. From all the available data it appears likely that liquids whose molecules have permanent dipoles do show a change with temperature in the pressure coefficient, but that for some, though certainly not all, non-polar liquids, having symmetrical molecules, the variation of the coefficient at constant volume is either non-existent or negligibly small.

Fig. 2.

Liquid isochores.



3. *The Energy–Volume Coefficient,* $(\partial E/\partial V)_T$.—This coefficient is the left-hand member of the so-called " thermodynamic equation of state : "

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P$$

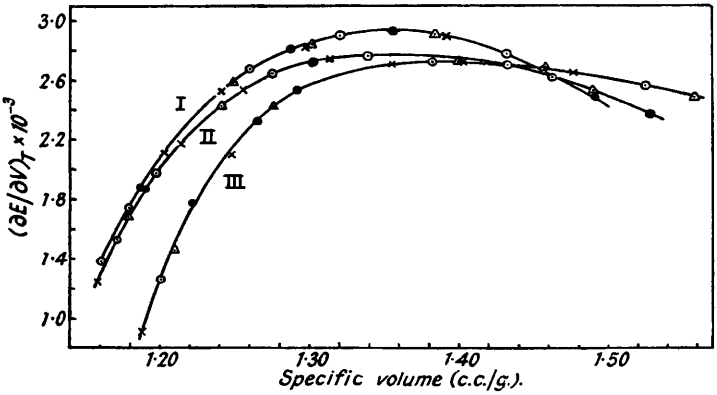
(E being the internal energy). When the pressure coefficient is a function of volume alone, $(\partial E/\partial V)_T$ is also necessarily a pure volume function. That this is so for the three normal hydrocarbons and their mixtures is shown in Fig. 3, where three typical curves are given for two pure liquids and one binary mixture. The points for the different temperatures all fall on one curve. Similar curves given by Gibson for his liquids show a displacement with temperature amounting to about 10% of the value of the energy–volume coefficient, for benzene and its derivatives between 25° and 65°, and about 6 or 7% for carbon tetrachloride. Water gives very much larger changes with temperature.

At a sufficiently high pressure the energy–volume coefficient passes through zero. Our pressure range does not include this point but, as Bridgman has found for other liquids, it appears to be at about 7000 atm., or somewhat higher. The preliminary decrease of $(\partial E/\partial V)_T$ through positive values up to this pressure implies that more energy flows out as heat to maintain isothermality than is put in as mechanical work, *i.e.*, the attractive forces in the liquid predominate. If the molecules are undeformable in this range, the molecular volume at the pressure at which $(\partial E/\partial V)_T = 0$ should be the same as that at 0° K. and 1 atm. Hildebrand (1929, *loc. cit.*) showed that this was so for ether, as far as can be estimated, and Bridgman (1931, *loc. cit.*) obtains a similar approximate equality for *n*-pentane. It may be expected that *n*-hexane, *n*-heptane, and *n*-octane would behave in the same way.

4. *The Attractive Internal Pressure.*—The equation of state $(\partial E/\partial V)_T = T\gamma - P$, in which, following Hildebrand, γ denotes $(\partial P/\partial T)_T$, has been combined by Gibson with Tait's equation constant B. The coefficient $(\partial E/\partial V)_T$ is regarded as being the sum of attractive and repulsive components $(\partial E_R/\partial V)_T + (\partial E_A/\partial V)_T$ and Gibson's identification of $B + P$ with the repulsive internal pressure leads to an expression for the attractive internal pressure $(\partial E_A/\partial V)_T = T\gamma + \mathrm{B}$.

FIG. 3.

Energy–volume coefficients.



I, n-*Octane.*
II, 22·04% *Octane*–77·96% *heptane.*
III, n-*Hexane.*

× 0°. ⊙ 25°. △ 40°. ● 60°.

This quantity is a pure volume function for most of the liquids investigated by Gibson and is expressible in the form a'/V^x, the exponent of V averaging 2·74 for benzene derivatives. We also obtain straight lines, including points at each temperature, for plots of log $(T\gamma + B)$ against log V. The slopes give an average value of $x = 3{\cdot}45$ for the pure liquids and their mixtures, and $a' \times 10^{-8}$ is repectively 0·4524, 1·494, and 1·191 for hexane, heptane, and octane. As Gibson has pointed out, it is unlikely that this relation holds down to the lowest pressures.

5. *The Volume Change on Mixing.*—The three normal paraffins investigated mix without expansion or contraction at all pressures and temperatures. An illustration is afforded by the following results for a 34·62% heptane–65·38% octane mixture at 25° :

Relative volumes.

Pressure (atm.)	1	1000	2000	3000	4000	5000
V (additive)	1·0295	0·9459	0·9016	0·8716	0·8480	0·8296
V (observed)	1·0296	0·9464	0·9016	0·8714	0·8484	0·8297

This behaviour may be contrasted with the divergencies found by Gibson and Loeffler (*J. Amer. Chem. Soc.*, 1939, **61**, 2877) for aniline–nitrobenzene mixtures.

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[*Received, June 7th,* 1951.]