Pressure–Volume–Temperature Relations in Solutions. II. The Energy–Volume Coefficients of Aniline, Nitrobenzene, Bromobenzene and Chlorobenzene

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Recent measurements have shown[1] that the compressions of benzene and a number of its monosubstituted derivatives over considerable ranges of pressure may be well represented by the Tait equation[2]

$$k = C \log [(B + P)/(B + P_0)] \qquad (1)$$

where k is the decrease in volume per unit volume when the pressure is raised from P_0 to P kilobars. B, a function of the temperature, is a constant characteristic of the liquid or liquid mixture, and C is a constant independent of temperature and the same for all the derivatives of benzene we have examined. In this paper we shall give data on the thermal expansions of the liquids mentioned in the title, give more complete compressibility data, and discuss some of the thermodynamic quantities derivable from these measurements, including the pressure–temperature coefficient $(\partial P/\partial T)_V$ which, following Hildebrand,[3] we shall denote as γ, and especially the energy–volume coefficient $(\partial E/\partial V)_T$.

Experimental

The compressions of the liquids to various pressures up to 1000 bars were measured at 25, 45, 65 and 85° in vitreous silica piezometers in our latest pressure apparatus,[4] and depend on the same constants for vitreous silica and mercury that were employed in the investigation of benzene.[5]

The specific volumes of the liquids at atmospheric pressure were measured at intervals of 10° between 25 and 85° in a weight dilatometer of the type used by Burlew[6] and by Pesce and Hölemann.[7] The dilatometer, made of vitreous silica, is shown diagrammatically in Fig. 1. Its chief merits are simplicity and ease of manipulation. By following Burlew's design of having the open end of the capillary above the dilatometer, we were able to avoid the complicated thermostat used by Pesce and Hölemann, and by having an opening at the top of the dilatometer bulb we were able to fill it readily with solutions whose

composition would have changed if evacuation had been necessary. The opening in the dilatometer was closed by a silica glass plate. The faces of this plate and of the supporting flange were ground flat and polished to an optical quality. No trouble from leakage occurred after we had acquired the technique of bringing the optically flat surfaces together. During an experiment the dilatometer was immersed in a well-stirred oil-bath and the tip of the capillary dipped into mercury contained in a small glass cup. The temperature was controlled "by hand" to ±0.01° and measured with the help of a 5-junction copper–constantan thermoelement[8] calibrated at the inversion point of sodium sulfate decahydrate (32.384°)[9] and at the steam point. The departures from L. H. Adams' table[10] were, respectively, +1 and −1 microvolt on the 5-junction element.
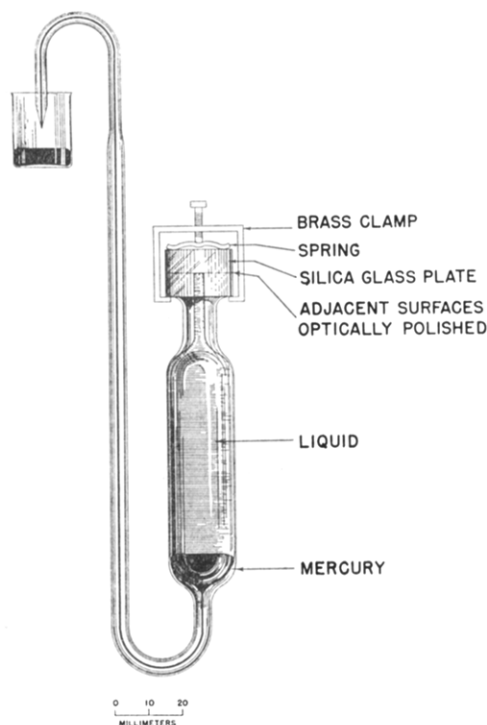

Fig. 1.—Diagrammatic sketch of weight-dilatometer made of vitreous silica for the determination of the thermal expansions of solutions over considerable temperature ranges.

After the temperature had been held constant (within 0.01°) for an adequate time, the small glass cup was

(1) R. E. Gibson and O. H. Loeffler, *J. phys. Chem.*, **43**, 207 (1939).

(2) This equation in the differential form was proposed by Tait in 1881 to fit the compressibility data for water. It was rederived by A. Wohl [*Z. physik. Chem.*, **99**, 234 (1921)], who applied it to some organic liquids, and it was later applied successfully to the existing data on a large number of liquids by H. Carl [*ibid.*, **101**, 238 (1922)], who showed that the constant C did not depend on the temperature.

(3) W. Westwater, H. W. Frantz, and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928).

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

(5) R. E. Gibson and John F. Kincaid, *ibid.*, **60**, 511 (1938).

(6) J. S. Burlew, *ibid.*, to be published.

(7) G. Pesce and P. Hölemann, *Z. Elektrochem.*, **40**, 1–5 (1934).

(8) R. E. Gibson and John F. Kincaid, THIS JOURNAL, **59**, 25 (1937).

(9) H. C. Dickinson and E. F. Mueller, *Bull. Bur. Standards*, **3**, 656 (1907).

(10) "International Critical Tables," Vol. I, p. 58.

removed and weighed. From the mass of mercury deposited in or taken from the cup during a given change of temperature, the thermal expansion was computed. Readings made with rising and with falling temperature indicated no hysteresis in the thermal expansion of the dilatometer itself. Over 10° intervals the thermal expansions were reproducible within 0.05%.

The volume of the dilatometer at different temperatures was determined from experiments with water and mercury confined in it, the volume–temperature data for these substances being taken from the "International Critical Tables."[11] After approximate corrections had been made for the volume of mercury in the emergent stem of the dilatometer, we computed the mean cubic expansion coefficients of vitreous silica in the form $(v_t - v_{25})/v_{25}(t - t_{25})$. At 45, 65, 85 and 95° this expression multiplied by 10^6 had the values: 1.43 (1.34), 1.46 (1.43), 1.57 (1.49), 1.63 (1.51). The figures in parentheses represent values of the same expression interpolated linearly from the mean coefficients of cubic expansion of vitreous silica given by Sosman.[12] The agreement is satisfactory.
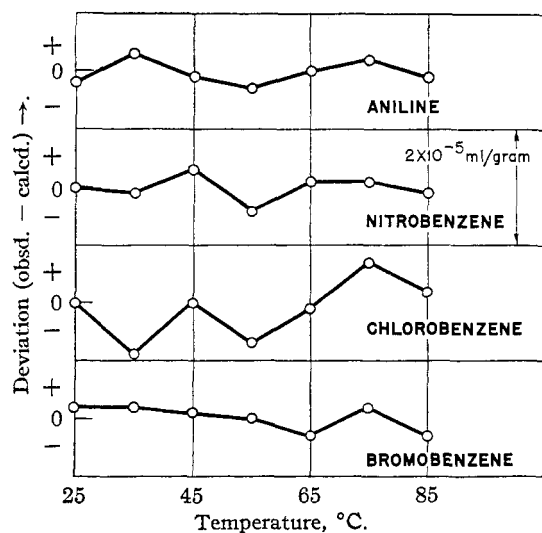

Fig. 2.—Differences between the observed thermal expansions of different liquids and those computed by cubic equations of the type of equation (2).

Aniline, nitrobenzene, chlorobenzene and bromobenzene were obtained from the Eastman Kodak Company. The three first-named were distilled under reduced pressure and the middle fractions were used. The original sample of bromobenzene was fractionated in a small column packed with glass beads. The second and third fractions were used. In Table I the specific volumes at 25° of the samples of liquid[13] we used are compared with apparently reliable ones found by other investigators. We concluded that the agreement indicated that our samples were sufficiently pure for the work in hand.

(11) "International Critical Tables," Vol. II, p. 548; Vol. III, p. 24.

(12) R. B. Sosman, "The Properties of Silica," Chemical Catalog Co., New York, 1927, p. 363.

(13) These specific volumes were determined in the usual way with U-tube pycnometers.

TABLE I

A COMPARISON OF THE SPECIFIC VOLUMES AT 25.00° OF THE LIQUIDS USED IN THIS WORK WITH DATA OF PREVIOUS INVESTIGATORS. THE FIGURES IN PARENTHESES ARE SPECIFIC VOLUMES AT 0°

Authors	Chloro-benzene	Bromo-benzene	Nitro-benzene	Aniline
Gibson and Loeffler	0.90818	0.67162	0.83451	0.98290
	(.88642)	(.65673)	(.81759)	(.96240)
Martin and Collie[a]	.90816	.67158		.98281
Martin and George[b]			.83438	
Timmermans and Martin[c]	.90834	.67193		
	(.88659)	(.65703)		
Albright[d]				.9828
Timmermans and Hennaut-Roland[e]			.83449	.98284
			(.81763)	(.96242)

[a] A. R. Martin and B. Collie, J. Chem. Soc., 2662 (1932).
[b] A. R. Martin and C. M. George, ibid., 1413 (1933).
[c] J. Timmermans and F. Martin, J. chim. phys., **23**, 733 (1926). [d] P. S. Albright, THIS JOURNAL, **59**, 2099 (1937).
[e] J. Timmermans and Mme. Hennaut-Roland, J. chim. phys., **32**, 589 (1935).

It was possible to use the dilatometer for direct measurements of the specific volumes of the liquids at 25°. Weighed amounts of mercury and solutions were introduced into the dilatometer and the whole warmed until the mercury completely filled the capillary. Mercury was then allowed to flow in from one of the weighed cups until the dilatometer and its contents were in equilibrium at 25.00°. From a knowledge of the total amount of mercury in the dilatometer, the mass of the solution—the total volume (determined from similar experiments with water)—it was easily possible to measure the specific volume to 1 in the fifth decimal place. At the end of each run all the mercury in the dilatometer was removed, cleaned and weighed. Such a method possesses distinct advantages when one is dealing with volatile liquids.

Results

The specific volumes were represented as functions of the temperature by cubic equations written for convenience in the form

$$v = v_{55} + a(t - 55) + b(t - 55)^2 + c(t - 55)^3 \quad (2)$$

TABLE II

COEFFICIENTS IN EQUATION 2 REPRESENTING THE SPECIFIC VOLUMES OF DIFFERENT LIQUIDS AS FUNCTIONS OF THE TEMPERATURE AT 1 ATMOSPHERE. THE CONSTANT v_{55} REFERS TO OUR SAMPLE (SEE TABLE I)

Substance	v_{55}	10^4a	10^7b	10^9c
Chlorobenzene	0.935873	9.589	13.229	4.38
Bromobenzene	.690481	6.498	7.602	1.875
Nitrobenzene	.855751	7.274	6.931	1.528
Aniline	1.008746	8.874	9.292	2.083

Our results are presented, therefore, in Table II, which gives the values of v_{55}, and the other coefficients in the equations for the four liquids. The excellent way in which these equations fit our data is shown in Fig. 2 where the differences between the observed specific volumes and those

calculated by equation (2) are plotted at different temperatures. It should be noted that the values of v_{55} refer to the samples we used. The expansion equations may be adapted to give the specific volumes of purer samples merely by adjusting the value of v_{55}. By differentiation of equation (2) we were able to compute the expansion coefficient $(\partial v/\partial T)_P$ at any temperature, and these computed values were used in any subsequent calculations without any reference to the deviations.

To test the validity of these equations for extrapolation beyond the observed range, we computed the specific volumes at $0°$, which are given in parentheses in Table I. These were compared with the measured values obtained by Timmermans and his colleagues, also in parentheses.

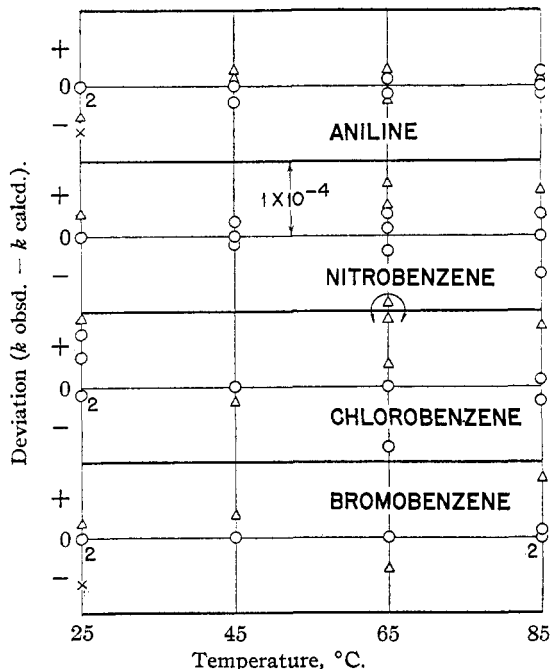The results of the compressibility experiments are summarized in Table III, which gives the

Fig. 3.—Differences between the observed compressions of different liquids and those calculated from the appropriate Tait equation (coefficients in Table III). The·open circles $\bigcirc$, triangles $\triangle$ and crosses $\times$ refer to compressions at 1000, 500 and 750 bars, respectively. All the experimental results except those of the compressions to 250 bars are included in the diagram.

TABLE III

CONSTANTS IN THE TAIT EQUATION FOR BENZENE AND SOME OF ITS DERIVATIVES AT DIFFERENT TEMPERATURES. FOR ALL THE LIQUIDS AT ALL THE TEMPERATURES $C = 0.2159_1$

Substance	25°	B in kilobars 45°	65°	85°
Benzene	0.970	0.829	0.701	
Chlorobenzene	1.249$_1$	1.097$_8$	0.960$_9$	0.835$_0$
Bromobenzene	1.404$_4$	1.247$_3$	1.103$_3$	0.972$_0$
Nitrobenzene	1.865$_2$	1.678$_8$	1.504$_5$	1.341$_6$
Aniline	2.006$_6$	1.798$_3$	1.605$_6$	1.429$_4$

values of B in the Tait equation for the different liquids at different temperatures, and in Fig. 3 where the deviations are plotted. It should be noted that although the chlorobenzene results at 500 bars deviated most widely, the values of the compressibilities at 1 atmosphere calculated from the Tait equation agreed within 1% with those obtained from sound velocities by Freyer, Hubbard and Andrews.[14] We already have commented[1] on the fact that the constant C has the value 0.2159_1 for all the liquids discussed in this paper and apparently it does not change with temperature.

The Pressure–Temperature Coefficient $(\partial P/\partial T)_V$.—To compute the coefficient $(\partial P/\partial T)_V$ at atmospheric pressure we used the relation

$$\gamma \equiv \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial v}{\partial T}\right)_P \Big/ \left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{v_t}\left(\frac{\partial v}{\partial T}\right)_P \times \frac{(B+P)}{0.4343C} \quad (3)$$

where v_t is the specific volume of the liquid at tem-

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

perature t and one bar pressure,[15] with the values of $(\partial v/\partial T)_P$ at 1 bar computed from equation (2). Two methods were used to compute $(\partial v/\partial T)_P$ at higher pressures. (a) The specific volumes at a given pressure were calculated from the compressions at each temperature, i. e., 25, 45, 65 and 85°, and then expressed as a function of temperature by empirical cubic or quadratic equations—the latter being quite adequate at the higher pressures. From these empirical equations $(\partial v/\partial T)_P$ was computed at each pressure. (b) From a consideration of the Tait equation it readily may be seen that

$$\left(\frac{\partial v}{\partial T}\right)_{P=P} = \left(\frac{\partial v}{\partial T}\right)_{P=P_0}(1-k) + \\ 0.4343Cv_t\frac{P}{B+P}\frac{1}{B}\left(\frac{dB}{dT}\right) \quad (4)$$

This equation enables us to compute the expansion coefficient at any pressure, $(\partial v/\partial T)_{P=P}$, if we know its value at 1 atmosphere (P_0), the constants

(15) The symbols generally used in this paper are summarized as follows. The specific volume is denoted by v, the molal volume by V, t is the temperature in °C., T the absolute temperature, E is the internal energy, P is the pressure in bars, 10^6 dynes/sq. cm., or kilobars, 10^9 dynes/sq. cm.

in the Tait equation and the change of B with temperature. This last quantity, which was obtained from empirical equations of the form

$$B = B_{25} + a_1(t - 25) + b_1(t - 25)^2 \quad (5)$$

values of a_1 and b_1 being given in Table IV for B

TABLE IV

COEFFICIENTS IN EQUATION 5 REPRESENTING B AS A
FUNCTION OF TEMPERATURE

Substance	B_{25}	$10^3 a_1$	$10^5 b_1$
Chlorobenzene	1.249$_1$	-7.89_7	1.6$_6$
Bromobenzene	1.404$_4$	-8.17_9	1.6$_2$
Nitrobenzene	1.865$_2$	-9.61_6	1.4$_8$
Aniline	2.006$_6$	-10.81_3	1.9$_9$

expressed in kilobars, is the weakest part of the whole calculation.[16] We used method (a) to compute $(\partial v / \partial T)_{P=P}$ at 1 bar and at 1000 bars, and method (b) at 250, 500, 750 and 1000 bars. Except in the case of chlorobenzene both methods gave essentially the same results.
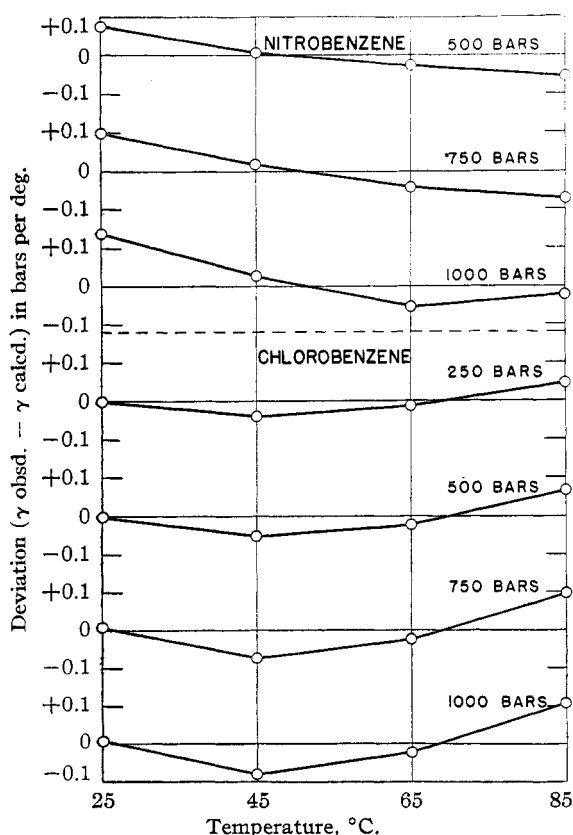

Fig. 4.—Deviations of the values of $(\partial P / \partial T)_V$ computed by the empirical equation (6) from the "observed" values.

(16) Carl[2] proposed the simple equation $B = T_c/T - constant$, where T_c is the critical temperature, to represent B as a function of T. This equation does not fit our data, and even if T_c is taken as an adjustable constant, it does not represent the data over the observed range as well as equation (5).

The coefficient γ increases with pressure at constant temperature, decreases with temperature at constant pressure, and decreases with temperature at constant volume. This last change is not large but is undoubtedly real and very significant. It is in accordance with Bridgman's general conclusions.[17]

We found empirically that the variation of γ over the temperature range at any pressure could be represented most simply by making γ a linear function of $(B + P)$, and, moreover, that the coefficient of $(B + P)$ is independent of pressure. At present no significance is attached to this relation, but to summarize our results in a concise and readily available form we give in Table V the constants l and m in the equation

$$\gamma = l + m(B + P) \quad (6)$$

TABLE V

CONSTANTS IN EQUATION 6 REPRESENTING THE PRESSURE-
TEMPERATURE COEFFICIENTS AS FUNCTIONS OF $(B + P)$
(SEE TABLE III)

		The coefficient l				
Substance	m	1 bar	250 bars	500 bars	750 bars	1000 bars
Chlorobenzene	8.17	2.85	1.59	0.28	-1.08	-2.47
Bromobenzene	7.79	2.65	1.42	.16	-1.14	-2.47
Nitrobenzene	7.35	2.73	1.56	.36	-0.86	-2.11
Aniline	7.37	3.43	2.29	1.12	$-.75$	-1.29

for the different liquids and a deviation curve in Fig. 4 for those cases where the difference between the observed and calculated values is greater than ± 0.04 bar/degree. The fact that equation (6) holds so well is interesting because it means that the expansion coefficient is simply related to B by equation (7)

$$\frac{1}{v_t}\left(\frac{\partial v}{\partial T}\right)_P = 0.4343 C \left\{ \frac{l}{(B + P)} + m \right\} \quad (7)$$

and, as the compressibility of the liquid is given by $0.4343 C / (B + P)$, it means further that over a range of temperature at a given pressure the expansion coefficient $(\partial v / \partial T)_P / v_t$ varies approximately linearly with the compressibility. The coefficient l as a function of the pressure decreases somewhat less rapidly than linearly as P increases. It is of interest to note that at constant volume the expansion coefficients $(\partial v / \partial T)_P$ and the compressibilities of all these liquids decrease as the temperature is raised.

The Energy–Volume Coefficient $(\partial E / \partial V)_T$

From the thermodynamic relation $(\partial E / \partial V)_T = T\gamma - P$ we computed the energy–volume coefficients for the various liquids at different temperatures and pressures. The results are given in

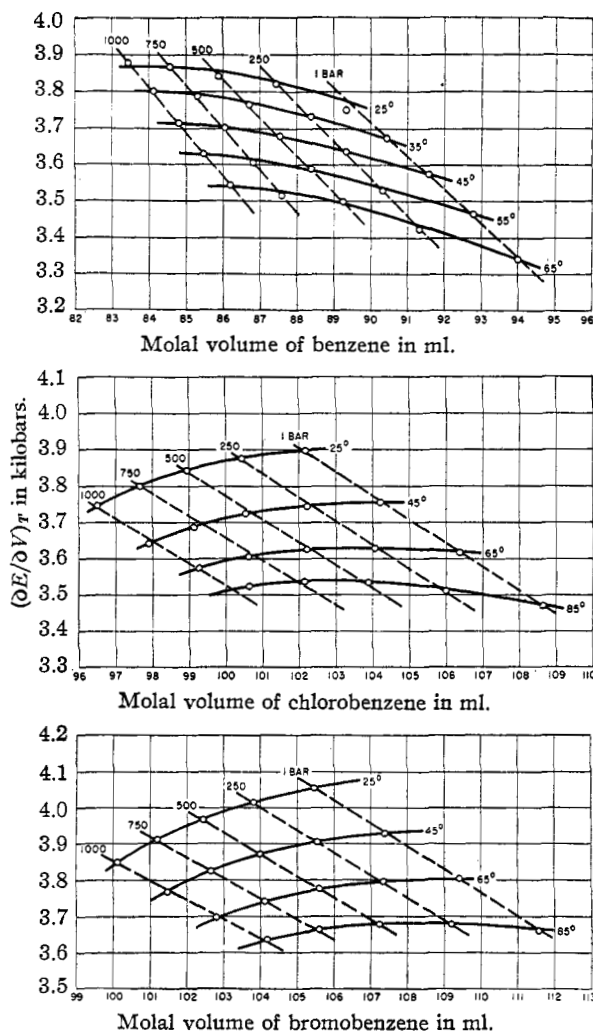(17) P. W. Bridgman, *Rev. Modern Phys.*, **1**, 12 (1935).

Fig. 5.—The internal pressures $(\partial E/\partial V)_T$ of benzene, chlorobenzene and bromobenzene as functions of the molal volumes at different temperatures.
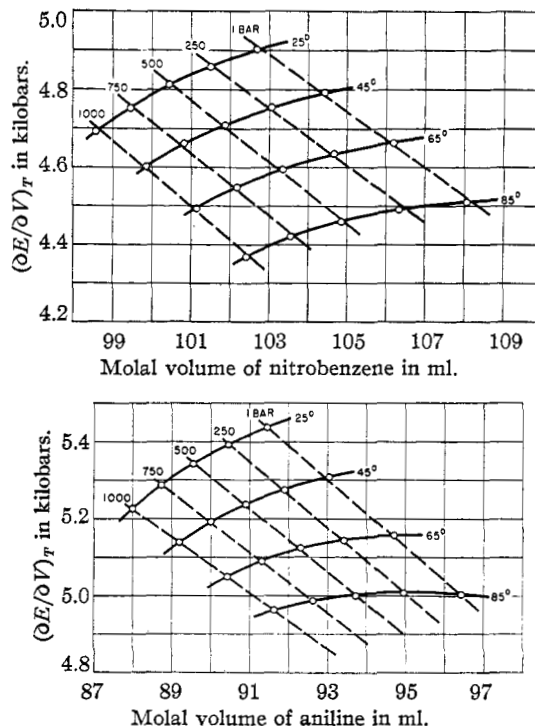

Fig. 6.—The internal pressures $(\partial E/\partial V)_T$ of aniline and nitrobenzene as functions of the molal volumes at different temperatures.

Figs. 5 and 6, where $(\partial E/\partial V)_T$ is plotted against the molal volume of the liquid, the isotherms and isobars being drawn. No special significance is attached to the apparent rectilinearity of the isobars. The results for benzene were computed from the data of Gibson and Kincaid.[5] We wish to call attention to two significant features of the curves in Figs. 5 and 6. (1) Our results cover the interesting but not much studied region in the neighborhood of the pressure and temperature where $(\partial^2E/\partial V^2) = 0$, a region where such simple formulas as $(\partial E/\partial V)_T = constant/V^n$ certainly do not apply.[18] (2) At constant volume $(\partial E/\partial V)_T$

diminishes as the temperature rises. The coefficient $(\partial E/\partial V)_T$ is positive and quite large for these liquids, ranging from 3.5 to 5.5 kilobars (84 to 131 cal. per cc.) and the changes of $(\partial E/\partial V)_T$ at constant volume illustrated in the diagrams are relatively small, being only about 10% of the total value. We believe, however, that these changes are real. At a given temperature $(\partial E/\partial V)_T$ increases from liquid to liquid in the order benzene, chlorobenzene, bromobenzene, nitrobenzene, aniline. The introduction of the polar group increases $(\partial E/\partial V)_T$ and at the same time makes $(\partial^2E/\partial V^2)_T$ more positive.

Where classical mechanics are applicable, the total energy of a fluid may be regarded as the sum of a term dependent only on the temperature, $E(T)$, the mean kinetic energy of the molecules at their equilibrium positions together with energy associated with rotation or internal degrees of freedom, and terms giving the potential energy due to intermolecular forces of attraction and repulsion,[19] E_A and E_R. Thus $E = E_R + E_A +$

(18) (a) J. H. Hildebrand, "The Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, 1936, p. 98; (b) J. Phys. Chem., **43**, 481 (1939); (c) Phys. Rev., **34**, 984 (1929); (d) P. W. Bridgman, ref. 17, p. 11; (e) O. K. Rice, J. Chem. Phys., **5**, 492 (1937).

(19) For expressions giving the energies of fluids containing spherical molecules see J. O. Hirschfelder and W. E. Roseveare, J. Phys. Chem., **43**, 15 (1939), or J. H. Hildebrand, ref. 18a, Chap. V. The authors express the total potential energy in terms of the potential energies of pairs of molecules and the distribution function for the molecules in the liquid. A fundamental treatment of the subject

$E(T)$ and $(\partial E/\partial V)_T = (\partial E_R/\partial V)_T + (\partial E_A/\partial V)_T$. If, following common usage,[20] we call $(\partial E/\partial V)_T$ the internal pressure P_i, we may call $(\partial E_R/\partial V)_T$ and $(\partial E_A/\partial V)_T$ the repulsive and attractive pressures P_R and P_A, respectively. It will be noted that P_R is negative and P_A is positive. In the region we are studying $-(\partial P_R/\partial V)_T$ increases more rapidly than $(\partial P_A/\partial V)_T$ as the volume is diminished along an isotherm and at the maximum where the observed $(\partial P_i/\partial V)_T = 0$, $(\partial P_A/\partial V)_T = -(\partial P_R/\partial V)_T$; at lower volumes further increase of repulsive pressure causes P_i to fall as the volume decreases.[21]

Our second observation that $(\partial E/\partial V)_T$ diminishes with temperature at constant volume is equivalent to the statement (which is obvious from Figs. 5 and 6) that $(\partial E/\partial V)_T$ increases more rapidly as the volume is diminished along an isobar than along an isotherm. We may explain this result by the hypothesis that increase of temperature increases the randomness of the distribution of the molecules in the liquid and that this increase of randomness increases the repulsive internal pressure. Lennard-Jones and Devonshire[22] have developed quantitatively the idea that when a solid melts the disorder introduced increases the free energy and causes an excess repulsive pressure. It is now generally assumed that the molecules are not distributed at random in a liquid, especially near its melting point, but that there persists an order (short range at least) in the arrangement of the molecules,[23] which is a function of pressure and temperature. As the temperature is raised the arrangement of the molecules in the liquid becomes more random.[23] If this happens when the volume of the liquid is kept constant, an additional disorder term is added to the repulsive pressure as in the melting phenomenon discussed by Lennard-Jones and Devonshire. The forces which determine the attractive pressure vary much less rapidly with distance than do those determining the repulsive pressures. It seems plausible to assume, therefore, that at constant volume the attractive pressure is unchanged by changes

in the molecular distribution function[24] and that it is the increase in repulsive pressure which lowers the observed value of $(\partial E/\partial V)_T$. In other words, a simple consequence of the decrease of $(\partial E/\partial V)_T$ with temperature at constant volume is that $(\partial^2 P/\partial T^2)_V$ is negative or that the $P-T$ curves at constant volume are concave to the temperature axis and that $T(\partial P/\partial T)_V$ rises less rapidly with temperature at constant volume than does the external pressure. This abnormal increase in the external pressure is a result of the increase in repulsive pressure due to increase of randomness.[25]

The Attractive Internal Pressure

From our previous work with the Tait equation[1,5] we have adopted the working hypothesis that $(B + P)$ at any pressure represents the difference between the thermal and attractive pressures or is equal to the repulsive pressure. It might be expected, then, that the increase of $(B + P)_V$ with temperature should just be equal to the decrease of $(\partial E/\partial V)_T$ with temperature at constant volume, and calculations show that this is approximately true in all the liquids we have studied. It will be seen at once that this result is expressed by the statement that $(T\gamma + B)$, which represents the attractive pressure P_A, is the same function of the volume for all temperatures, and, indeed, we have found that we may express $(T\gamma + B)$ in the form $a'V^{-n}$ over the whole range of pressures and temperatures we have investigated. In Fig. 7 we have plotted $\log (T\gamma + B)$ against $\log V$, the slopes of the curves give $-n$ and the intercepts on the ordinates give $\log a'$. It will be seen that the

has been given by J. G. Kirkwood [*J. Chem. Phys.*, **3**, 300 (1935)]. A complete formula for a mixed fluid in which the relative orientations of the molecules are taken into account is given by G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

(20) T. W. Richards, THIS JOURNAL, **46**, 1419 (1924).

(21) For discussions of the complete $(\partial E/\partial V)_T$–$V$–curves for liquids, see J. H. Hildebrand, ref. 18a, Chap. V; O. K. Rice, *J. Chem. Phys.*, **5**, 492 (1937).

(22) J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.* (London), **A169**, 317 (1939).

(23) J. D. Bernal, *Trans. Faraday Soc.*, **33**, 27 (1937).

(24) Changes in the relative orientation of the molecules may produce changes in the attractive potential energy at constant volume. This will be discussed later.

(25) That the repulsive potential energy of a liquid increases with temperature at constant volume may also be seen from the following considerations. It has been found convenient and, indeed, necessary in the explanation of many phenomena in fluids to assume that the repulsive energy of a pair of molecules rises rapidly as the molecules approach one another but that the slopes of the repulsive energy-distance curves are not infinite as would be the case for hard spheres [P. W. Bridgman, ref. 17, p. 10; J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937)]. This is all that is implied by the brief but loose statement that it is assumed that the molecules are compressible. Hence, as their kinetic energy increases, the distance of closest approach of the molecules decreases. Curves giving the distribution functions of the atoms in liquid potassium [C. D. Thomas and N. S. Gingrich, *J. Chem. Phys.*, **6**, 411 (1938)] and sodium [F. H. Trimble and N. S. Gingrich, *Phys. Rev.*, **53**, 278 (1938)] show that the probability of finding atoms at very short distances from a given atom increases as the temperature increases. As the repulsive potential energy varies exponentially with the distance between molecules, it must rise considerably as the probability of finding molecules at short distances increases. It is not yet clear, however, how this temperature effect is modified by volume changes.

points for all temperatures lie substantially on the same straight line.[26]

It will be seen that n is approximately the same for aniline, nitrobenzene, bromobenzene and chlorobenzene, the slopes of the curves being -2.70, -2.69, -2.78 and -2.78, respectively. These give an average of -2.74 so that we may write

$$P_A = (T\gamma + B) = a'V^{-2.74} \qquad (8)$$

The values of $10^{-6}\, a'$ for P in kilobars and V in cc. per mole are as follows: chlorobenzene, 1.621; bromobenzene, 1.870; nitrobenzene, 2.163; aniline, 1.730. The curve for benzene, which is not a straight line, indicates that n diminishes as the volume increases. Over most of the range we have studied, however, P_A for benzene is given by $3.38 \times 10^6/V^3$, indicating that at low volumes the attractive potential energy is proportional to V^{-2}, which is in qualitative agreement with the theory of van der Waals forces.[27] In the polar derivatives the longer-range forces may be responsible for making the exponent of V less than that of benzene. It is certain that the linear relation between $\log (T\gamma + B)$ and $\log V$ does not hold over a large range of volume for any of these liquids. At high volumes the attractive pressure in fluids is proportional to $1/V^2$ no matter what the law of force is.[28] The quantity $E_A = -V(T\gamma + B)/1.74$ should be larger than the heat of evaporation of the liquid, as it neglects entirely the repulsive potential energy. Actually E_A so computed is lower than the values of the heat of evaporation given in the literature, although these are not concordant,[29] indicating that P_A decreases less rapidly at the higher volumes than it would if equation (8) held over the whole range.

In the study of benzene[5] it was pointed out that $(B + P)_V$ was a linear function of the temperature

(26) In this work we are dealing with molecules that are not spherically symmetrical and are also polar. Doubtless changes in the orientation of the molecules occur as the temperature is changed, but our results indicate that changes in P_A arising from changes in orientation make a contribution to the change of $(\partial E/\partial V)_T$ with temperature at constant volume which is small compared with the contribution due to the distribution of the molecules. We find, however, that at constant volume $(T\gamma + B)$ decreases slightly with temperature, indicating a possible decrease of P_A due to change in the distribution function, but the difference is so close to the over-all uncertainty of our calculations that further discussion of it is undesirable. For instance, in the extreme case of nitrobenzene $(\partial E/\partial V)_T$ for $v = 0.8345$ decreases by 525 bars from 25 to 85°, whereas under the same conditions $(T\gamma + B)_V$ decreases by 104 bars. With other liquids the total change in $(T\gamma + B)_V$ over the same temperature range was less than 50 bars.

(27) See F. London, Trans. Faraday Soc., **33**, 8 (1937).

(28) See J. A. Beattie and Oscar C. Bridgeman, Proc. Am. Acad. Arts Sci., **63**, 239 (1928).

(29) See table by J. H. Hildebrand, ref. 18a, p. 104; G. Scatchard, Chem. Rev., **8**, 329 (1931).

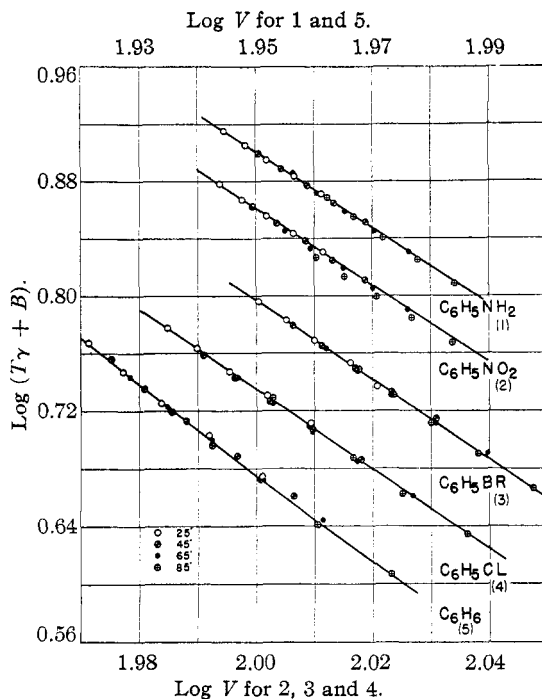

Log V for 1 and 5.

Log V for 2, 3 and 4.

Fig. 7.—The logarithm of the attractive internal pressures of different liquids as functions of the logarithm of the molal volume. Note the points at different temperatures all lie on one curve for each liquid.

and that the extrapolated values of $(B + P)_V$ at 0°K. were approximately inversely proportional to the square of the volume. Over the range we have investigated, $(B + P)_V$ is also a linear function of T for nitrobenzene, but the extrapolated values at 0°K. increase as the volume increases. It will be noticed that the slopes of the $(\partial E/\partial V)_T$ $-V$ curves for these two substances are opposite in sign. For the other liquids $(B + P)_V$ is not a linear function of the temperature, the slope decreasing as the temperature is raised. From the foregoing argument it will be seen that where $(B + P)_V$ increases linearly with T, $(\partial E/\partial V)_T$ decreases linearly with T at constant volume. The linear relation we found holds because over a relatively short range of temperature the "disorder" part of the repulsive pressure is proportional to the thermal energy of the molecules.

A consideration of Figs. 5 and 6 suggests that, for a given change in volume, variation of temperature at constant pressure produces a larger change in the distribution of molecules in a liquid than does the corresponding variation of pressure at constant temperature. The coefficient $(\partial P/\partial T)$ along the melting curve might be regarded as

a measure of the change in pressure which must be applied to counteract the change in randomness produced by a given rise of temperature. Here we may suppose that the distribution of the molecules is constant, being that existing in the crystal. We have recently measured $(\partial P/\partial T)_V$ for solid benzene; it is approximately 23 bars per degree. The coefficient $(\partial P/\partial T)$ along the melting curve is approximately 36 bars per degree.[30] For a given rise of temperature, the pressure change necessary to keep constant the distribution in the solid is, according to this argument, more than 1.5 times the pressure change required to keep constant the volume of the solid.

Summary

From measurements of the specific volumes at 25°, the thermal expansions and the compressions of aniline, nitrobenzene, chlorobenzene and bromobenzene, we have been able to compile a table of the volumes of these liquids at any temperature and pressure in the region 25 to 85° and 1 to 1000 bars. Suitable equations for computing the first and second derivatives also are given. From

(30) R. E. Gibson, THIS JOURNAL, **56**, 5 (1934); L. Deffet, *Bull. soc. chim. Belg.*, **44**, 71 (1935).

these data the coefficients $(\partial P/\partial T)_V$ and $(\partial E/\partial V)_T$ were computed. Our data enable us to discuss the variation of these and other thermodynamic functions with temperature at constant volume. Both $(\partial P/\partial T)_V$ and $(\partial E/\partial V)_T$ decrease as the temperature increases at constant volume. It is suggested that this effect is due to an increase in the repulsive internal pressure which follows from an increased randomness in the distribution of the molecules in the liquids at higher temperatures. The quantity $(B + P)$ in the Tait equation for the compressibility of the liquids is identified empirically as the repulsive internal pressure. It increases with temperature at constant volume and, when it is combined with the total internal pressure, an estimate of the attractive pressure is made. The attractive pressure so computed is expressible as $P_A = a'V^{-n}$ and is dependent only on the volume within the limits of our experimental error. The exponent n has the value 3 for benzene and 2.74 for the polar liquids.

A weight dilatometer of vitreous silica suitable for the rapid and precise measurements of the thermal expansions of solutions is described.

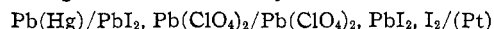# A Lead–Iodine Voltaic Cell

BY W. C. VOSBURGH AND VERNON H. DIBELER

Among the cells made by Gerke[1] the cell

$$Pb(Hg)/PbI_2, Pb(ClO_4)_2/Pb(ClO_4)_2, PbI_2, I_2/(Pt)$$

is outstanding in that its temperature coefficient $(\Delta E/\Delta T)$ is as small as that of the saturated Weston cell and the two cells that he made agreed unusually well. These results suggested that the cell might have some value as a standard cell. A number of cells were made and they agreed unusually well with Gerke's cells. They were constant in electromotive force as long as observed and were superior to the Weston cell with respect to recovery from polarization.

The cells were set up in vessels of the type used by Vosburgh and Craig.[2] Lead amalgam, about 5% lead, was prepared electrolytically. In some of the cells a more dilute amalgam was used by mistake. The iodine was resublimed. Lead iodide and lead chloride were pre-

(1) Gerke, THIS JOURNAL, **44**, 1684 (1922).
(2) Vosburgh and Craig, *ibid.*, **51**, 2012 (1929).

cipitated from dilute solutions. Lead nitrate was recrystallized. Lead perchlorate solution was prepared by the addition of an excess of lead oxide to a perchloric acid solution, followed by filtration and the addition of enough perchloric acid to give a clear solution.

In the construction of the iodine electrodes, equal quantities of dry lead iodide and iodine were ground, mixed thoroughly and placed in one leg of the cell vessel. Lead perchlorate solution was then introduced to a depth of several centimeters and then lead iodide was allowed to fall through the solution to form a layer about one centimeter thick above the iodine–iodide mixture. A platinum electrode sealed into the end of a glass tube was then introduced carefully into the mixture. In some of the cells a platinum wire in the form of a helix was used for the electrode, but usually the electrode was of platinum foil about 1 sq. cm. in total surface area. The area of the amalgam electrode was about 1 sq. cm. also.

The cells may be divided into three groups. In the first group, Cells 3–16, the materials were not free from oxygen, and air was not excluded. Six of these cells agreed well with each other. *Four others were rejected*