[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

Pressure–Volume–Temperature Relations in Solutions. V. The Energy–Volume Coefficients of Carbon Tetrachloride, Water and Ethylene Glycol

BY R. E. GIBSON AND O. H. LOEFFLER

In earlier papers of this series[1] we have attempted to correlate the effect of temperature at constant volume on certain thermodynamic properties of liquids with changes in molecular distribution in the liquids. The behavior of the energy–volume coefficient $(\partial E/\partial V)_T$ under such conditions is especially illuminating and indeed one might well use this coefficient and its change with temperature at constant volume as criteria of the "normality" of the liquid.[2] In order to develop this idea further we have examined a "normal" liquid[3] whose molecules possess spherical symmetry, *viz.*, carbon tetrachloride; a liquid whose behavior is notoriously abnormal but whose practical importance is large, *viz.*, water; and ethylene glycol, a liquid which dissolves electrolytes almost as readily as water but which gives solutions whose properties indicate that the complications due to changes of molecular distribution in aqueous solutions are of only minor significance in glycol solutions.[4] In this paper we shall present the new data on the thermal expansions and compressions of these liquids, together with readily derived thermodynamic quantities, and point out some conclusions deducible from our results.

Experimental

Baker and Adamson reagent carbon tetrachloride was fractionated in a small column packed with glass beads. The middle fraction, whose specific volume at 25° was 0.63108, was used. This specific volume agrees well with the corresponding value of 0.63111 given by Timmermans and Martin[5] and of 0.63126 given by Scatchard, Wood and Mochel.[6] It should be noted that our value of the specific volume was obtained when the liquid was introduced into the pycnometer at a temperature just slightly below its boiling point. If the liquid was allowed to cool before being placed in the pycnometer, we obtained specific volumes clustering around 0.63118, much closer to the value given by Scatchard and his collaborators. We think the difference is due to dissolved air, a conclusion to which we shall refer later under the measurements of the thermal expansions. Ethylene glycol from the Eastman Kodak Company was distilled over potassium hydroxide and redistilled *in vacuo*. The specific volume of the distillate was 0.90101 at 25°, a value which agrees well with 0.90101 which we published some years ago after repeated efforts to purify glycol.[4] The original samples were purchased over an interval of four years.

The thermal expansions were measured in our vitreous silica weight dilatometer, with the usual technique, precautions and precision.[1a] The only incident of note in these measurements occurred with carbon tetrachloride. With a sample that had been boiled and cooled before it was introduced into the dilatometer we were unable to get up to 65° without the appearance of bubbles, and at 70° all the liquid was forcibly ejected from the dilatometer by vapor, even though the normal boiling point of the liquid is 76.8°. If, however, the dilatometer was filled with boiling carbon tetrachloride, expansion measurements up to 74° could be made with ease. The specific volumes of carbon tetrachloride were measured at 10° intervals from 15 to 75° and those of ethylene glycol from 25 to 105°.

The compressions of the liquids from 1 to 250, 500, 750 and 1000 bars were measured at different temperatures between 25 and 105° in a pressure apparatus fitted with windows for visual observation.[4] Two new vitreous silica piezometers, differing from those we have already described[7] only in the feature that the reëntrant tubes are quite straight and end in finer orifices, were used for these measurements. The capacities of the piezometers were 9.569 and 9.662 ml. at 25°. Because of the low thermal expansion of vitreous silica, the fractional change in the volume of the piezometer from 25° to the highest temperature, 105°, was only 1.2×10^{-4}, which is insignificant for our compression results. We also assumed that the compressibility[8] of vitreous silica, $\frac{1}{v_0}\left(\frac{\partial v}{\partial P}\right)_T$, was 2.76×10^{-6} reciprocal bars and was independent of pressure and temperature over our working range. These assumptions were made because the data on the compressibility of vitreous silica, and particularly on its variation with pressure and temperature, are not good enough to justify any others. Indeed, apparently reliable values of the compression of vitreous silica[8] from 1 to 1000 bars range between 2.76×10^{-3} and 2.58×10^{-3}.

A small but annoying source of uncertainty in the use of this type of piezometer arises from the fact that at the beginning of a compression experiment the mercury may

---

(1) R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **61**, (a) 2515, (b) 2877 (1939).

(2) For recent discussions of "normal" and "associated" liquids see R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," The Macmillan Company, New York, N. Y., 1939, p. 319; J. H. Hildebrand, *J. Chem. Phys.*, **7**, 233 (1939).

(3) See, however, Hildebrand, previous ref.

(4) R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **59**, 579 (1937); R. E. Gibson, *ibid.*, **59**, 1521 (1937).

(5) J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926).

(6) G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **61**, 3206 (1939).

(7) R. E. Gibson, *ibid.*, **57**, 284 (1935); Fig. 1.

(8) L. H. Adams and R. E. Gibson, *J. Wash. Acad. Sci.*, **21**, 381 (1931); P. W. Bridgman, *Am. J. Sci.*, **10**, 363 (1925); F. Birch and R. R. Law, *Bull. Geol. Soc. Am.*, **46**, 1219 (1935); F. Birch and R. B. Dow, *ibid.*, **47**, 1235 (1936).

not be flush with the tip of the capillary at the lower end of the reëntrant tube in the piezometer. There is a tendency for the liquid in the piezometer to produce a slight depression in the mercury as it comes to temperature equilibrium. By observing in each experiment the pressure required to fill the reëntrant tube with mercury we were able to minimize this uncertainty in one of two ways. (1) If a reliable form of pressure-volume equation for the liquid was known it was possible to compute the effective volume of the capillary from the above-mentioned pressure observation and the observed compression between this pressure and the highest pressure reached in the run. (2) When the pressure required to fill the reëntrant tube with mercury was plotted against the reciprocal of the approximate value of the compression obtained from our experiments, it was found that the points for a given liquid or series of related liquids at the different temperatures scattered closely around a straight line for any particular piezometer. With repetitions and measurements of compressions to different pressures a large number of points were obtained and the best straight line was drawn through them. A correction for the volume of the capillary was applied to those measurements whose points departed significantly from this line. In this way the scattering of the compression results was reduced to the uncertainty of the pressure reading, *viz.*, ±0.5 bar. In making these low-pressure measurements (50 to 200 bars) we checked the manganin wire resistance gage against a special Bourdon test gage over a period of a year. It is of interest to note that the manganin gage proved itself to be highly reliable (±0.5 bar) in this low-pressure region.

Results

Thermal Expansions.—Between 15 and 75° the specific volumes of carbon tetrachloride are given in terms of equation (1) obtained from the data by the method of least squares and the deviation curve in Fig. 1. This is the mean of four different expansion experiments.

$$v = 0.647091 + 8.282 \times 10^{-4}\,(t - 45) + 14.776 \times 10^{-7}\,(t - 45)^2 + 4.5 \times 10^{-9}\,(t - 45)^3 \quad (1)$$

The deviations are all in the sixth decimal place and are practically insignificant. The absolute values of the specific volumes given by equation (1) depend on the assumption that the specific volume of carbon tetrachloride at 25.00° is 0.631082. It is obvious, however, that equation (1) may be modified to conform with any other probable value of the specific volume at 25° merely by an additive correction to the first term.

Over the range 25 to 105° the specific volumes of ethylene glycol are given by equation (2), also obtained by the method of least squares, and the deviation curve in Fig. 1.

$$v = 0.924848 + 6.2796 \times 10^{-4}\,(t - 65) + 9.2444 \times 10^{-7}\,(t - 65)^2 + 3.057 \times 10^{-9}\,(t - 65)^3 \quad (2)$$

Here again the deviations are insignificant. The thermal expansibilities $(\partial v/\partial T)_P$ of the two liquids may be obtained from equations (1) or (2) by simple differentiation.

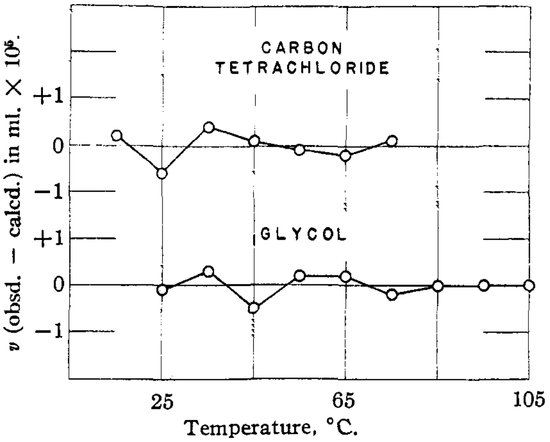

Fig. 1.—Differences between the observed specific volumes of carbon tetrachloride and glycol and those computed by equations (1) and (2), respectively.

Compressions.—The compression results were adequately represented by the Tait equation[1a]

$$k = C \log\,[(B + P)/(B + P_0)] \qquad (3)$$

for all three liquids.[9] The coefficients in equation (3) are listed in Table I and the deviations $(k_{\text{obsd.}} - k_{\text{calcd.}})$ are plotted in Figs. 2 and 3. In the diagram for water two sets of determinations are listed. The circles indicate our new results, the dots indicate results obtained with a different

TABLE I

CONSTANTS IN THE TAIT EQUATION (EQUATION 3) FOR CARBON TETRACHLORIDE, WATER AND GLYCOL AT DIFFERENT TEMPERATURES

Temp., °C.	*B* in kilobars Carbon tetrachloride (C = 0.21290)	Water (C = 0.3150)	Ethylene glyco (C = 0.21763)
25	0.8670	2.996	2.544
35	.8005	3.055	
45	.7377	3.081	2.363
55	.6785	3.078	
65	.6221	3.052	2.186
75		3.005	
85		2.939	2.011
105			1.840

---

[9] The symbols used in this paper are as follows. The molal energies and volumes are denoted by E and V, respectively, and the corresponding lower-case symbols represent specific quantities. All volumes are in milliliters. P is the pressure, T the absolute temperature and t the temperature in °C. The compression $-\Delta v/v_0$ is represented by k, the subscript zero refers to atmospheric pressure at any temperature. The quantity $(\partial P/\partial T)_V$ is represented by γ. C_V is the molal heat capacity at constant volume, and C_P the molal heat capacity at constant pressure.

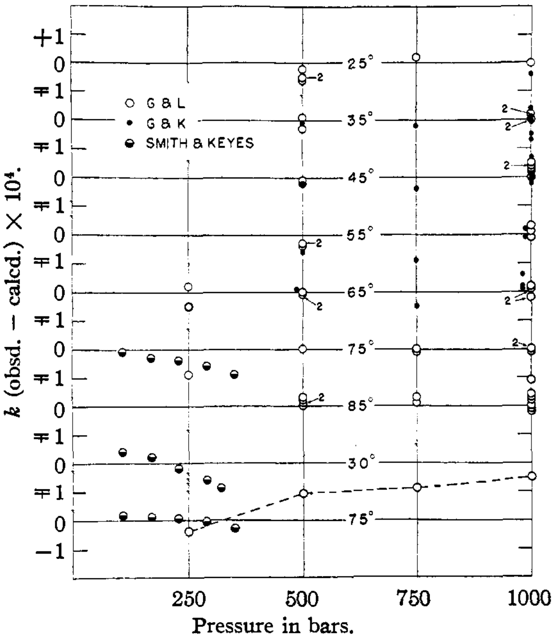

Fig. 2.—Differences between the observed compressions of water and those computed from the Tait equation with the constants in Table I. G and L refer to the results obtained in this work, G and K to results obtained in 1937. The lowest deviation curve gives differences between the values computed with equation (4), and those observed by Smith and Keyes at lower pressures and those reported in this paper at higher pressures (broken line). The numeral 2 adjacent to certain points indicates two separate measurements which gave identical results.

piezometer during our work on benzene[10] in the summer of 1937. The points at 1000 bars and 25° on this diagram are the means of 10 and 11 separate experiments, respectively.

Within the precision of our observations the coefficient C is independent of temperature for carbon tetrachloride and for glycol. We have also assumed it to be independent of temperature for water, although a careful analysis of the data indicates that there may be a slight variation of C with temperature and possibly also with pressure. Although we made very few measurements below 500 bars, we have used the Tait equation down to 1 bar and it is, therefore, of interest to compare our interpolations by means of the Tait equation with the very careful observations of Smith and Keyes[11] in the region 1 to 350 bars. In Fig. 2 we have plotted the deviations between Smith and Keyes' experimentally *observed* compressions (p. 301 of their paper) from approximately 4 bars to the pressure indicated, and those computed by the Tait equation with our coefficients at 75° and at 30°. These are represented by the half-shaded circles in the sixth and eighth deviation curves and it will be seen that the agreement is very good except at 350 bars. In the ninth deviation curve on this diagram we show the deviations of Smith and Keyes' results (half-shaded circles) and of our results (dotted line) from the equation

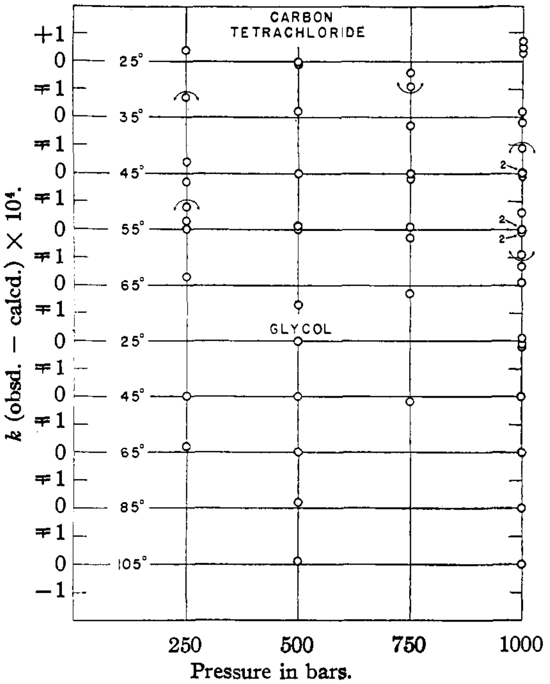

Fig. 3.—Differences between the observed and calculated compressions of carbon tetrachloride and glycol. The calculated compressions were obtained from Tait equations with constants in Table I. The numeral 2 adjacent to certain points indicates two separate measurements which gave identical results.

$$k = 0.31566 \log [(3.0258 + P)/(3.0268)] \qquad (4)$$

whose coefficients were determined from the Smith and Keyes data at 75°. It will be noted that this equation gives a residual at their highest pressure (350 bars) which is one-tenth as large as Smith and Keyes obtained with their own equation, and that when extrapolated to 1000 bars this equation gives a compression which is 1.5×10^{-4} smaller than ours. This agreement is satisfactory, particularly in view of the fact that our results depend on the compression of vitreous silica which introduces an uncertainty that may make them too large by as much as

---

(10) R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **60**, 511 (1938).

(11) L. B. Smith and F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934).

1.8×10^{-4} at 1000 bars. The compressibilities of water computed from our results by the Tait equation do not agree at all well with the *smoothed* values given by Smith and Keyes (Table VI of their paper). For example, they place the minimum compressibility of water between 25 and 30°, whereas we place it very close to 50°, a value which agrees with older results.[12] The compressions of glycol at 25° agree within experimental error with those we published in 1937 when allowance is made for the fact that we now use 0.03935 rather than 0.03930 for the compression of water to 1000 bars.

Calculations of the Energy–Volume Coefficients

The well-known equations

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P, \text{ and}$$
$$(\partial P/\partial T)_V = -\left(\frac{\partial v}{\partial T}\right)_P \Big/ \left(\frac{\partial v}{\partial P}\right)_T$$

formed the basis for the computation of the energy–volume coefficients. The compressibility coefficient $(\partial v/\partial P)_T$ was computed at each pressure and temperature from the appropriate Tait equation, the residuals being neglected. At atmospheric pressure the expansion coefficients of carbon tetrachloride and glycol were obtained by differentiation of equations (1) and (2). The expansion coefficients of water were taken from the fourth paper of this series.[13] The expansion coefficients $(\partial v/\partial T)_P$ at the higher pressures were computed from those at 1 bar, the constants in the Tait equations and the variation of B with temperature by means of an equation we have already published.[14] Values of (dB/dT) at different temperatures were computed for carbon tetrachloride, water and glycol from equations (5), (6) and (7), respectively.

$$B = 0.8670 - 0.006808(t - 25) + 0.00001713(t - 25)^2 \quad \mathrm{CCl_4} \quad (5)$$

$$B = 2.996 + 0.007585(t - 25) - 0.0001790(t - 25)^2 + 0.000000613(t - 25)^3 \quad \mathrm{H_2O} \quad (6)$$

$$B = 2.544 - 0.009134(t - 25) + 0.0000042(t - 25)^2 \quad \text{glycol} \quad (7)$$

The expansion coefficients of carbon tetrachloride at 1000 bars were checked by passing an equation through the specific volumes at this pressure. The agreement was good (within 1%) and it is of interest to note that $(\partial^2 v/\partial T^2)$ and hence $(\partial C_P/\partial P)$ is zero at this pressure.

From these computations we obtained tables of $(\partial v/\partial T)_P$ and $(\partial v/\partial P)_T$ and hence $(\partial P/\partial T)_V$, $(\partial E/\partial V)_T$ and $C_P - C_V$ at any pressure and temperature in the range we covered. The results are shown in Figs. 4, 6 and 7, where $(\partial E/\partial V)_T$ is plotted against the molal volume of the liquid.[15]

In order to check our calculations we made two series of direct measurements of $(\partial P/\partial T)_V$ for carbon tetrachloride by enclosing the liquid over mercury in a glass vessel and observing the change of pressure required to keep the volume constant when the temperature was changed. These results, covering a range from 25 to 85°, never deviated from those computed from the expansion coefficients and the compressibilities by more than 1% and seldom by more than 0.5% of $(\partial P/\partial T)_V$.

Discussion of Results

Carbon Tetrachloride.—It has been generally assumed that the energy–volume coefficient of a normal liquid is a function of the volume only, but Fig. 4 shows that this property of carbon tetrachloride decreases slightly but significantly when the temperature is raised at constant volume. The decrease is about two-thirds as great as that observed in benzene[1a] over the same range of temperature. In our paper on benzene and its derivatives[1a] we ascribed this effect to

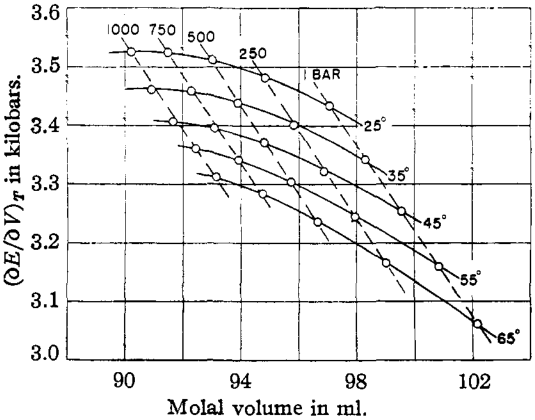

Fig. 4.—The energy–volume coefficients of carbon tetrachloride as functions of the molal volume at different temperatures.

---

[12] See N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corporation, New York, N. Y., 1940, p. 243.

[13] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, 63, 443 (1941).

[14] Ref. 1a, eq. (4).

[15] Tables giving numerical values of the volumes, compressions, compressibilities, thermal expansibilities, pressure–temperature coefficients, energy–volume coefficients, $(C_P - C_V)$, may be obtained from the American Documentation Institute, 2101 Constitution Avenue, Washington, D. C., remitting 27¢ for microfilms or 90¢ for photocopies.

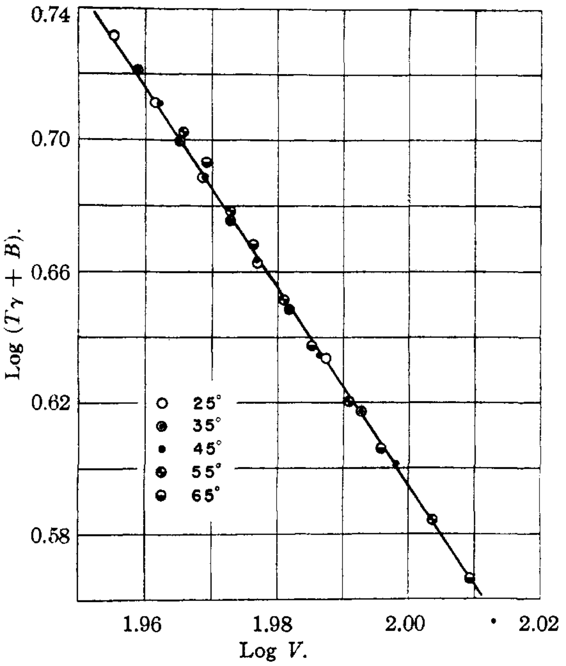

Fig. 5.—The logarithm of the attractive component of $(\partial E/\partial V)_T$ for carbon tetrachloride as a function of the logarithm of the molal volume. Note the points at different temperatures all fall on the same line.

the increase in the repulsive component[16] of $(\partial E/\partial V)_T$ produced by an increase in the randomness in the molecular distribution in the liquid. A simpler and better explanation, adumbrated in footnote 25 of that paper, is as follows. The potential energy of a given liquid depends on the total volume of the liquid, which fixes the mean distance between molecular centers, and on a distribution function $W(r)$ which gives the probability that two molecules will be found separated by a distance r.[17] If the molecules are compressible,[18] $W(r)$ may vary with temperature at constant volume in a normal liquid because the distance of closest approach of a pair of molecules will depend on the velocity with which they collide. At higher temperatures, therefore, $W(r)$ for very small values of r increases, and consequently E_R, which varies exponentially with r, and $(\partial E_R/\partial V)_T$, which varies in the same way, also increase. On the other hand, E_A and its derivatives, varying less rapidly with r, depend almost entirely on the mean value of r, that is, on the volume. Since $(\partial E_R/\partial V)_T$ and $(\partial E_A/\partial V)_T$ have opposite signs, their sum, $(\partial E/\partial V)_T$, will decrease with temperature at constant volume in accord with our observations. Indeed it may be affirmed that the normal behavior of $(\partial E/\partial V)_T$ for actual liquids is similar to that shown in Fig. 4.

Following the analysis given in our previous paper we have assumed that $(B + P)$ in the Tait equation represents $(\partial E_R/\partial V)_T$ and hence computed $(\partial E_A/\partial V)_T = T\gamma + B$. The result is a quantity which is a function of the volume only, as may be seen from Fig. 5. From the constants of the linear relation between log $(\partial E_A/\partial V)_T$ and log V shown in this diagram, it was found that $(\partial E_A/\partial V)_T = 3.94 \times 10^6/V^3$ over a 13% change in volume.

Water.—It is apparent from Fig. 6 that the energy–volume coefficient of water behaves in an entirely different way from that of carbon tetrachloride. Instead of decreasing slightly with rise of temperature at constant volume, it increases more than 300% from 25 to 85°, and it is well known that $(\partial E/\partial V)_T$ is actually negative for water below 4°. The temperature coefficient of $(\partial E/\partial V)_T$ for a given volume decreases as the temperature rises, but even at 85° it is large enough to indicate that from the thermodynamic standpoint water is by no means normal below 150°, a conclusion which has been reached on

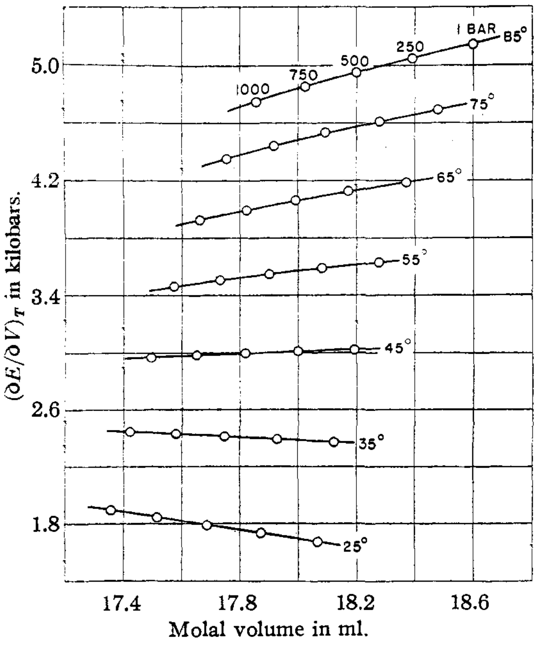

Fig. 6.—The energy–volume coefficients of water as functions of the molal volume at different temperatures.

---

[16] It is convenient to divide the energy of a liquid into three parts: $E(T)$, a function of temperature only, E_A, the potential energy due to attractive forces, and E_R, the potential energy due to repulsive forces. A similar division may be made for the energy-volume coefficients, $(\partial E(T)/\partial V)_T$ being, of course, zero.

[17] For references see ref. 1a, footnote 19.

[18] See ref. 1a for a definition of this term.

evidence from diverse sources,[19] although statements that water behaves like other liquids above 50° are still made.[20] Another significant feature of Fig. 6 is the fact that the slopes of the isotherms are negative at low temperatures and become positive at the higher temperatures, the reverse of what happens with normal liquids.

Material for a qualitative explanation of the results in Fig. 6 is contained in the current theory of the molecular distribution in water.[21] The low coördination number (approximately 4) of the molecules in water, known from careful studies of X-ray diffraction patterns,[21] is strong evidence that directed bonds between the water molecules tend to hold them in an open structure. When the liquid is compressed at constant temperature a crushing of the open structure occurs, molecules being forced into spaces they normally cannot enter without acquiring enough energy to strain or break hydrogen bridges.[22] Inspection of a model of the tetrahedral packing in ice shows that hydrogen bridges must be strained or broken when the structure is crushed.[23] It will be recalled that the viscosity of water[24] decreases when it is compressed isothermally below 35°, a fact which confirms the hypothesis that hydrogen bridges are broken by compression.

In correlating the peculiar behavior of the energy–volume coefficient of water with the extent of the tetrahedral arrangement in the liquid, we may write

$$(\partial E/\partial V)_T = (\partial E_A/\partial V)_T + (\partial E_R/\partial V)_T + (\partial E_H/\partial V)_T \qquad (8)$$

where $(\partial E_A/\partial V)_T$ is the component arising from ordinary non-directed attractive forces, $(\partial E_R/\partial V)_T$ is the component due to repulsive forces between the molecules, and $(\partial E_H/\partial V)_T$ is the component due to the straining or breaking of hydrogen bridges when the structure is crushed, and we must note that $(\partial E_R/\partial V)_T$ and $(\partial E_H/\partial V)_T$ are negative while $(\partial E_A/\partial V)_T$ is positive. We must also use the plausible and well-justified assumption that $(\partial E_H/\partial V)_T$ is proportional to the extent of the tetrahedral arrangement actually present in the liquid which increases as the temperature falls[25] or the volume increases. Thus $(\partial E_H/\partial V)_T$ decreases numerically when the temperature is raised at constant volume or when the pressure is raised at constant temperature. Furthermore, the temperature coefficient of $(\partial E_H/\partial V)_T$ decreases with rise of temperature or isothermal rise of pressure.

These considerations explain the relative positions of the curves in Fig. 6. For instance, although rise of temperature at constant volume causes a slight numerical increase in $(\partial E_A/\partial V)_T$ and $(\partial E_R/\partial V)_T$ because the average coördination number rises, the net effect on these terms is small, but this change of conditions causes a significant numerical decrease in $(\partial E_H/\partial V)_T$ with the result that $(\partial E/\partial V)_T$, the observed quantity, increases. We shall show later that the magnitude of $(\partial E_H/\partial V)_T$ required to explain the experimental results is not unreasonable.

Equation (8) also accounts for the anomalous slopes of the curves in Fig. 6. The maxima on the curves of $(\partial E/\partial V)_T$ *vs.* V for ordinary liquids arise from the fact that $(\partial E_R/\partial V)_T$ increases numerically much more rapidly than $(\partial E_A/\partial V)_T$ when the volume diminishes, $(\partial E_R/\partial V)_T$ representing the change in repulsive potential energy when the molecules are forced to interpenetrate each other. Inspection of equation (8) suggests that the sum of the two terms $(\partial E_R/\partial V)_T$ and $(\partial E_H/\partial V)_T$ corresponds to the repulsive term in the relation for normal liquids. At low temperatures $(\partial E_H/\partial V)_T$ is the predominating term and instead of increasing rapidly on compression, it actually diminishes slightly, thus offsetting the rapid increase in $(\partial E_R/\partial V)_T$. Equation (8) leads to the conclusion, therefore, that the effect of the term $(\partial E_H/\partial V)_T$ is to push the maxima on the $(\partial E/\partial V)_T$—$V$ isotherms to lower volumes than would be observed if the tetrahedral packing were not present in water. The effect of temperature on $(\partial E_H/\partial V)_T$, just discussed, accounts for the appearance of the normal slopes of the curves in Fig. 6 at the higher temperatures in the volume range covered by our results.

We may estimate the required magnitude of $(\partial E_H/\partial V)_T$ by extrapolating the plot of $(\partial E/\partial V)_T$ against its temperature coefficient along an isochore to the point where the temperature coeffi-

---

[19] (a) P. C. Cross, J. Burnham and P. A. Leighton, THIS JOURNAL, **59**, 1134 (1937); (b) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

[20] D. D. Eley, *Trans. Faraday Soc.*, **35**, 1431 (1939).

[21] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933); J. Morgan and B. E. Warren, *ibid.*, **6**, 666 (1938); S. Katzoff, *ibid.*, **2**, 841 (1934).

[22] The term hydrogen bridge is used here in the customary sense to mean directed, short-range O-H-O intermolecular linkages between water molecules.

[23] See discussion of the structure of Ice II and the Ice I–Ice II transition by R. L. McFarlan, *J. Chem. Phys.*, **4**, 60 (1936).

[24] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **61**, 86 (1925).

[25] See, for example, the relative heights of the peaks at 4.5 Å. on Morgan and Warren's distribution curves.

cient vanishes. It may be assumed that the value of $(\partial E/\partial V)_T$ at this point is the value it would have were water a normal liquid and that the difference between $(\partial E/\partial V)_T$ at any temperature along this isochore and this extrapolated value represents $(\partial E_H/\partial V)_T$. At $V = 18.12$ we found the extrapolated value of $(\partial E/\partial V)_T$ to be 6300 bars or 151 cal. per cc., and at the same volume $(\partial E_H/\partial V)_T$ had the values 111, 78, 53 and 33 cal. per cc. at 25, 45, 65 and 85°, respectively.

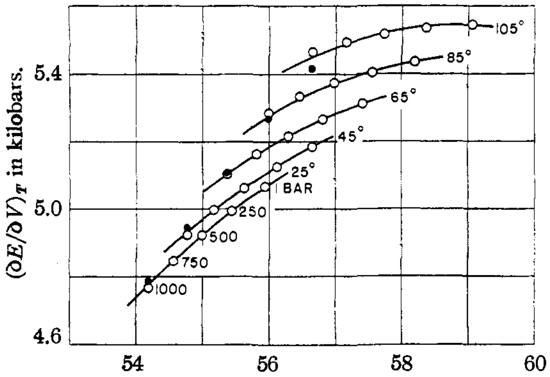

Fig. 7.—The energy–volume coefficients of glycol as functions of the molal volume at different temperatures. The dots indicate values computed from an expansion equation passed directly through the volumes at 1000 bars.

At 25° the internal energy due to hydrogen bridges in water is approximately 7 to 9 kcal. per mole.[26] Our calculation indicates, therefore, that when the volume of 1 mole of water is reduced by 1 cc. (requiring a pressure of about 1.5 kilobars), the increase in energy arising from the straining or breaking of the hydrogen bridges is between 1 and 2% of the total energy due to hydrogen bridges, a very reasonable result. According to our results for the normal liquids, it would be better to determine the value of $(T\gamma + B)$ under the conditions where its temperature coefficient vanishes, assume that this quantity is independent of temperature at constant volume and hence compute $(\partial E_H/\partial V)_T$. When this calculation is made, the estimate of $(\partial E_H/\partial V)_T$ at 25° is 146 cal./cc., which leaves the result substantially the same. We do not emphasize this method of calculation, however, first because of some dubiety in the interpretation of B for water, and second because we have not taken into account the effect of change of coördination number on the various terms in equation (8), especially on the repulsive term.

Glycol.—Figure 7 shows that the energy–volume coefficient of glycol, like that of water, increases with temperature at constant volume. The magnitude of the temperature coefficient of $(\partial E/\partial V)_T$ at constant volume is, however, so much smaller than the corresponding quantity for water that we feel justified in assuming that structural changes in glycol play only a secondary role in determining the variation of its thermodynamic properties with temperature, pressure and the addition of dissolved substances.

The existence of directed intermolecular bonds in hydroxylic liquids is well established[26a] but, although these bonds are strong, the geometry of the molecules does not allow them to produce a tetrahedral arrangement in the liquid, water being unique in this respect. It is to the tetrahedral structure produced by hydrogen bonding, rather than to the bonding itself, that we must attribute the peculiar thermodynamics of water, and it is, therefore, not surprising that glycol should show these peculiarities to such a small extent, even though its viscosity and high boiling point indicate very strong intermolecular bonding. The fact that glycol does resemble water in some degree (*cf.* Figs. 6 and 7) suggests that the intermolecular bonding in the liquid does produce a slightly open structure possibly by the formation of zigzag chains branched in space.

Specific Heats at Constant Volume.—From the thermodynamic identity $(\partial C_V/\partial V)_T = (\partial(\partial E/\partial V)_T/\partial T)_V = T\,(\partial^2 P/\partial T^2)_V$ it will be seen that the variation of $(\partial E/\partial V)_T$ with temperature we have been discussing is really just $(\partial C_V/\partial V)_T$. For carbon tetrachloride, benzene and its derivatives $(\partial C_V/\partial V)_T$ is negative, *i. e.*, C_V increases on isothermal compression. Kincaid and Eyring[27] have called attention to this fact in connection with benzene and attributed it to changes in the potential restricting rotation in the liquid. The explanation we have just given for the behavior of $(\partial E/\partial V)_T$ and hence of $(\partial C_V/\partial V)_T$ does not involve restricted rotation but what may be called "hindered translation." The interpenetration of molecules on collision associates a certain amount of potential energy with the translational degrees of freedom and results in a contribution to C_V.[28] The more the liquid is com-

---

(26) (a) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 281; (b) J. D. Bernal and R. H. Fowler, *op. cit.*; (c) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

(27) J. F. Kincaid and H. Eyring, *J. Chem. Phys.*, **6**, 620 (1938).

(28) See (a) J. F. Kincaid and H. Eyring, *op. cit.*, p. 625; (b) J. *Chem. Phys.*, **5**, 587 (1937).

pressed (at a given temperature) the greater is the average time a molecule spends in collision with its neighbors and consequently the greater is this contribution to C_V.[29] Further confirmation of this hypothesis is given by the fact that C_V for benzene increases with rise of temperature at constant volume.[30] This hypothesis also accounts for the fact that C_V for liquids is much greater than for the corresponding ideal gases even at the critical temperature where hypotheses of restricted rotation become improbable.[28b] Although the volumes of liquids are relatively large under these conditions, the temperatures are high enough to make the hindered translation appreciable. It would be expected that C_V would fall to the ideal gas value only when the volume is so large that the probability of molecular collisions becomes very small.

In water $(\partial C_V/\partial V)_T$ is positive and diminishes rapidly with temperature, that is to say, C_V decreases on compression but at a diminishing rate as temperature rises. It should be noted that C_V for water also decreases continuously as the temperature rises both at constant pressure and at constant volume. The relatively large value of C_V for water arises from the heat absorbed when hydrogen bridges are broken by rise of temperature. Since this extra absorption of heat is proportional to the extent of tetrahedral coördination in water, it will be seen that the explanation we have given for the behavior of the energy–volume coefficient is consistent with the variations of C_V with volume and temperature. In glycol $(\partial C_V/\partial V)_T$ behaves in the same way as it does in water. Figure 7 suggests, however, that it is possible that $(\partial C_V/\partial V)_T$ increases with temperature, a fact which may be significant, but as the change is just on the limits of precision of our data, we shall not discuss it here.

Expansion Coefficients at Constant Pressure and Constant Volume.—Figure 8 gives a comparison of the expansion coefficients of the liquids as functions of the temperature at constant pressure and at constant volume. Normal behavior is seen in the curves for carbon tetrachloride and glycol where the isobars have positive slopes and are convex toward the temperature axis, whereas the isochores have negative slopes. In water, however, the isobar and the isochore are practically indistinguishable between 25 and 50°; if there is a difference, the isochore lies above the isobar. A moment's reflection will show that the peculiar behavior of water exhibited by these curves is explicable in terms of the theory of the molecular distribution in water and its change with temperature which we have discussed, the low expansion coefficient of water at the lower temperatures arising from the possibility of "internal expansion."

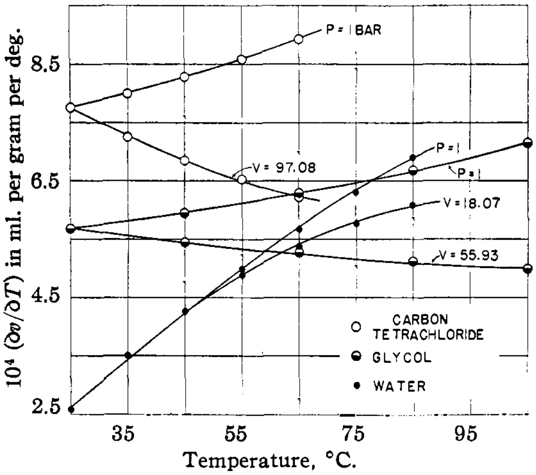

Fig. 8.—A comparison of the thermal expansibilities of carbon tetrachloride, water and glycol as functions of temperature at constant pressure and at constant volume.

The behavior of the energy–volume coefficient of water, especially its change of sign, suggests the customary designation of $(\partial E/\partial V)_T$ as the "internal pressure" of the liquid cannot be applied in this case. An analysis shows that it is only when $(\partial E/\partial V)_T$ is strictly a pure volume function that we can identify it with the internal pressure and retain any physical significance in the term. In the interests of clarity, therefore, we suggest that the application of the designation "internal pressure" to $(\partial E/\partial V)_T$ be discontinued.

Summary

From new measurements of the specific volumes at 25°, the thermal expansions and the compressions, we have been able to compile a table of the volumes at any temperature and pressure in the range 25 to 65° and 1 to 1000 bars for carbon tetrachloride and in the range 25 to 105° and 1 to 1000 bars for ethylene glycol. A

---

(29) It will be seen that this is equivalent to saying that compression reduces the flat portion on the dynamic potential energy curves of Kincaid and Eyring (ref. 28b, p. 588).

(30) This result is obtained when the values of C_V for benzene computed by Kincaid and Eyring (Table VI of the paper cited), due allowance for the internal degrees of freedom having been made, are plotted against the volumes given by Gibson and Kincaid (THIS JOURNAL, 60, 511 (1938)).

similar table covering the range 25 to 85° and 1 to 1000 bars has been compiled for water, older values of the expansions and new measurements of the compressions being used. Suitable equations for computing the first and second derivatives are given, the Tait equation always being used for the pressure–volume relations. The thermal expansibilities, the compressibilities, the pressure–temperature coefficients, the energy–volume coefficients, $(C_P - C_V)$ and other related properties have been computed.

The energy–volume coefficients of carbon tetrachloride decrease slightly with rise of temperature at constant volume. This is regarded as the normal behavior of actual liquids and is explained in terms of the effect of change in molecular distribution on the repulsive component of $(\partial E/\partial V)_T$. A pure volume function, tentatively identified with the attractive component of $(\partial E/\partial V)_T$, is obtained when $(\partial E/\partial V)_T$ is combined with the constant B of the Tait equation. The energy–volume coefficients of water behave quite differently from those of other liquids, but all the differences may be accounted for by the addition of a term which gives the change in hydrogen bonding energy in the liquid with volume. The magnitude of the term is reasonable. Qualitatively the $(\partial E/\partial V)_T - V$ diagram for ethylene glycol resembles that of water, but the increase of $(\partial E/\partial V)_T$ with temperature at constant volume is so much less that we feel justified in assuming that distribution changes in glycol and glycol solutions have only a minor effect on the volume properties of these liquids.

The effect of temperature on the energy–volume coefficients of the liquids discussed is correlated with the variation with volume of their specific heats at constant volume. A comparison of the thermal expansibilities of the liquids at constant pressure and at constant volume is also made.

Several refinements in the technique of measuring compressions by the piezometer method are described.

WASHINGTON, D. C. RECEIVED DECEMBER 11, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BUFFALO]

The Chain Carriers in Eder's Reaction

BY G. H. CARTLEDGE

The oxidation of oxalates by mercuric chloride according to the reaction

$$K_2C_2O_4 + 2HgCl_2 \longrightarrow 2KCl + Hg_2Cl_2 + 2CO_2$$

has been the subject of numerous investigations since Eder's studies on its use in actinometry.[1] The most important facts derived from these investigations may be summarized as follows. (1) The reaction proceeds at room temperature only when the solution is illuminated or supplied with a suitable chemical inductor, such as potassium permanganate. (2) The reaction occurs photochemically when the illumination contains no more ultraviolet light than is able to pass through glass (even window panes), although the reacting solution is colorless and the only components absorbing in the visible region of the spectrum are the traces of impurities remaining. The reaction occurs readily in ultraviolet light and under X-radiation.[2,3] (3) The photochemical reaction is extremely sensitive to inhibitors and catalysts. Oxygen is a strong inhibitor to both the dark and photochemical reactions[2,4,5,6]; numerous fluorescing dyes and potassium trioxalatocobaltiate[5] are examples of positive catalysts. These appear to act as photosensitizers in the photochemical reaction. (4) The order of the reaction depends upon the conditions.[7] The reaction has a chain mechanism, Roseveare[2] having found a very large quantum yield with X-rays. The temperature coefficient of the photochemical reaction varies between 1 and 2 for different wave lengths.[8] (5) In the dark, the reaction may be induced by addition of very small amounts of strong oxidizing agents such as potassium permanganate, manganese dioxide, and the oxalato complexes of trivalent manganese or cobalt. Ferrous salts alone do not induce the reaction, but if oxygen also is present, the higher

---

[1] Eder, *Ber.*, **13**, 166 (1880).

[2] Roseveare, THIS JOURNAL, **52**, 2612 (1930).

[3] Wyckoff and Baker, *Am. J. Roentgenol. Radium Therapy*, [6], **22**, 551 (1929).

[4] Jodlbauer and Tappeiner, *Ber.*, **38**, 2602 (1905).

[5] Cartledge and Djang, THIS JOURNAL, **55**, 3214 (1933).

[6] Roseveare and Olson, *ibid.*, **51**, 1716 (1929).

[7] Cartledge and Goldheim, *ibid.*, **55**, 3583 (1933).

[8] Padoa and Minganti, *Atti accad. Lincei*, **24**, II, 97 (1915).