JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 62 APRIL 5, 1940 NUMBER 4

[JOINT CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY AND THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Measurement of the Heat Capacity of a Small Volume of Liquid by the Piezo-thermometric Method.[1] I. Apparatus for Measuring $(\partial T/\partial P)_S$ and Results for Benzene and Toluene

BY JOHN S. BURLEW[2]

The Piezo-thermometric Method

Precise measurements of the heat capacity of pure organic liquids at frequent intervals over a wide range of temperature are of prime importance in the formulation and testing of a comprehensive theory of the liquid state. In order that compounds difficult and expensive to prepare may be highly purified before use in such an investigation, small samples are desirable. Adiabatic calorimetry, which heretofore has been the most precise method of measuring the heat capacity of liquids, requires a fairly large sample, especially if the heating interval is small, which it should be if the results are to be of any value whatever. The method described in the present series of papers was developed for the purpose of measuring precisely and conveniently the heat capacity of only 5 ml. of a liquid over a wide range of temperature using a cooling interval of 0.4°.

This method involves two independent sets of measurements for the evaluation of the two differential coefficients in equation (1)[3] at the same

$$c_p = T\frac{(\partial V/\partial T)_P}{(\partial T/\partial P)_S} \qquad (1)$$

absolute temperature T. For convenience in reference, I call it "the piezo-thermometric method" because the two principal measurements in the determination of the adiabatic temperature-pressure coefficient $(\partial T/\partial P)_S$ are those of pressure and temperature. Although this quantity is a derivative, it must be measured as the quotient of a finite change of temperature by a finite change of pressure. The coefficient of thermal expansion $(\partial V/\partial T)_P$ is obtained by differentiation of an empirical equation used to express measured values of the specific volume of the liquid as a function of temperature.

Joule[4] had used equation (1) as the basis of an experimental verification of the second law of thermodynamics. Although several later experimenters measured $(\partial T/\partial P)_S$ of various substances at relatively high pressures, only in recent years has it been measured in order to determine c_p of a liquid. Dixon and Rodebush[5] measured

---

(1) The application of this method to a small volume of liquid was described first in a dissertation accepted by The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934. The next year the apparatus was rebuilt at Yale University, and certain refinements were made in it. The apparatus and technique as herein described are those that were used at Yale University. They were described before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 26, 1935.

(2) Sterling Fellow in Chemistry, Yale University, 1934–1936; present address: Geophysical Laboratory, Washington, D. C.

(3) The units in equation (1) are: c_p (the heat capacity) in decijoules per degree per gram, $(\partial V/\partial T)_P$ in cubic centimeters per degree per gram, and $(\partial T/\partial P)_S$ in degrees per bar. For the derivation of this equation from the first and second laws of thermodynamics, see G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, eq. 25, p. 137.

(4) J. P. Joule, *Phil. Mag.*, **17**, 364 (1859).

(5) A. L. Dixon and W. H. Rodebush, THIS JOURNAL, **49**, 1162 (1927).

$(\partial T/\partial P)_S$ of molten sodium, potassium, and lead; and Richards and Wallace[6] measured $(\partial T/\partial P)_S$ of five organic liquids. Then they computed c_p, using values of $(\partial V/\partial T)_P$ taken from the literature. In neither case was an effort made to use small samples.

An apparatus for the measurement of $(\partial T/\partial P)_S$ of 5 ml. of a liquid is described in the present paper; and a new type of weight dilatometer for the measurement of $(\partial V/\partial T)_P$ of this same quantity of liquid is described in the one[7] that follows. The values of the heat capacity resulting from a combination of the data obtained with these two pieces of apparatus in the case of benzene and of toluene are given in a third paper.[8]

Apparatus

Pressure System.—The manner of controlling and measuring the pressure is illustrated in Fig. 1. Compressed nitrogen was stored at convenient working pressures in a gas bottle (volume, 400 ml.), to which was connected a pressure distributor supported by cross-bars 7 cm. above the surface of the oil in a thermostat. The bomb (Fig. 2) that contained the piezo-thermometric cell was suspended in the thermostat by a short pipe by means of which it was connected to the under side of the pressure distributor. The release of pressure was very quick because the bore of this pipe was 6 mm. and the holes in the hollow-stem release valve were 3 mm. in diameter. A handle on the release valve enabled it to be opened by a single rapid motion of the operator's hand.

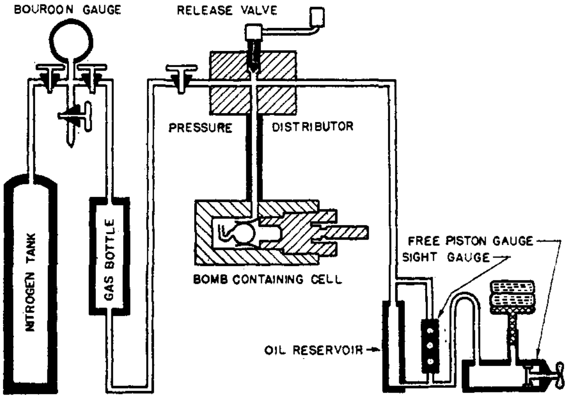


Fig. 1.—Pressure system of the piezo-thermometric apparatus (schematic).

A fourth connection from the pressure distributor led to a free piston gage[9] through an oil reservoir (volume, 50 ml.) and a U-trap. These accessories were needed in order to prevent nitrogen from blowing past the shallow layer of oil[10] in the cylinder of the gage. The level of oil in the reservoir could be adjusted by means of a screw, and the slight hydrostatic pressure from it could be measured to ±1 millibar by means of a sight gage.

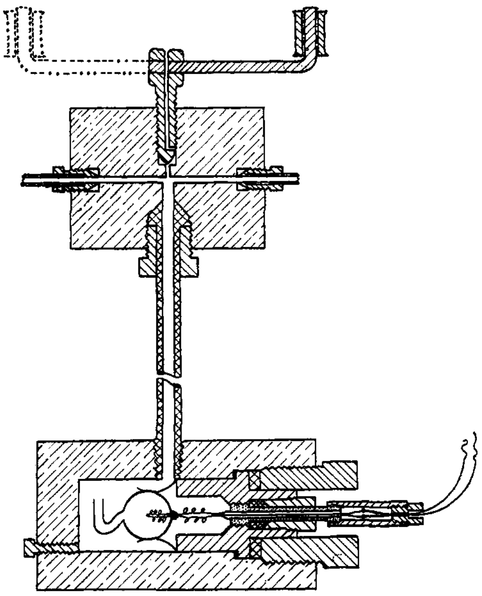


Fig. 2.—Piezo-thermometric cell in bomb attached to pressure distributor (scale, $^1/_4$).

The nominal multiplier ratio of the free piston gage was 16:1. A measurement of the piston diameter with a micrometer agreed with this value within the manufacturer's tolerance limits of ±0.1%. The corresponding gage constant for local gravity in New Haven (980.28 cm./sec.^{2}) was 2.431 bars per kilogram, and its probable error was assumed to be ±0.05%, half the tolerance limits. When the temperature of the gage changed 4.5°, the gage constant changed 0.01%. For the few measurements during which the temperature of the gage differed this much from ordinary room temperature (21°), a correction was applied to the observed pressure.

The masses of the weights were determined in terms of a 100-g. weight that had been calibrated at the Bureau of Standards. As a result of the calibration the mass of each weight was known with a maximum uncertainty of ±0.001%. The height at which the weights were rotated was kept the same in all experiments.

Thermostat.—The fluctuations of the temperature of the 65-liter oil-bath in which the piezo-thermometric bomb was immersed had to be less than ±0.005° in order not to interfere with the measurement of $(\partial T/\partial P)_S$. This degree of regulation was obtained by means of an intermittent bare nichrome heater that was controlled by a thermoregulator made of a long glass tube wound in a helix around a central U-tube and filled with xylene and mercury. Sticking in the capillary was prevented by having the electrical contact with the mercury made at a

---

[6] W. T. Richards and J. H. Wallace, This Journal, **54**, 2705 (1932).

[7] J. S. Burlew, *ibid.*, **62**, 690 (1940).

[8] J. S. Burlew, *ibid.*, **62**, 696 (1940).

[9] A commercial "dead-weight gage tester" manufactured by the Consolidated Ashcroft-Hancock Co., Inc.

[10] The oil used was Wyrol, similar in properties to Nujol. It was colored red with an aniline dye (special oil-soluble cardinal dye No. A45035, distributed by National Aniline and Chemical Co.) to render it visible in the sight gage.

point of tangency[11] of a bent piece of No. 32 nichrome wire.

A heater wrapped on the bomb pipe just above the surface of the oil was used to block off heat leak. Without the heater the leak was so great that at 80° the bomb could remain indefinitely at a temperature 1° lower than that of the thermostat.

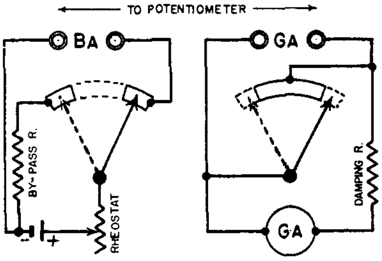


Fig. 3.—Short-circuiting switch for the thermel-galvanometer circuit. (The two contacts rotated simultaneously on a common shaft.)

The temperature of the thermostat up to 80° was measured with a mercury-in-glass thermometer graduated on the stem in 1/10° in accordance with the specifications of the Bureau of Standards. It was calibrated against a platinum resistance thermometer[12] used in conjunction with a Mueller resistance bridge[12] at 5° intervals in the oil thermostat under exactly the same conditions as later prevailed during use. In order to avoid large stem corrections, temperatures from 80 to 110° were measured with another platinum resistance thermometer. The resistance thermometers were calibrated at the ice and steam points. It is believed that the temperature observations had a probable error of ±0.02° up to 50°; ±0.03° from 50 to 80°; and ±0.02° from 80 to 110°.

Potentiometric System.—The potentiometer, a "thermofree" instrument built to order by the Leeds and Northrup Company, had a range of 550 microvolts in steps of 5 microvolts. The circuit was similar to that in the lower decades of the White potentiometer made by the same company. The battery current was balanced against a self-contained standard cell by means of an auxiliary pointer galvanometer, the sensitivity of which was great enough to permit adjustment to ±0.03%, as determined by a test. The maker's calibration showed that the resistances had been adjusted to their nominal values with an uncertainty of less than 0.1%.

The galvanometer, a Leeds and Northrup narrow-coil, type HS instrument with a period of 6.1 sec., was packed in cotton wool in a wooden box and was mounted 3.15 meters from a ground-glass scale. It was used critically damped, and the working sensitivity then was 16 mm. per microvolt.

The potentiometer was housed in a dry air thermostat at 25°. A wooden cover protected the switches on top of the potentiometer from drafts. The storage battery was kept in a wooden enclosure. The electrical system was separated from its surroundings by a double equipotential shield.[13] The steel pressure bomb was made part of the outer grounded shield. Even in damp weather the parasitic electromotive force did not exceed 0.1 microvolt, and it showed no sudden changes.

A duplex short-circuiting switch (Fig. 3) obviated opening or closing the galvanometer circuit during the course of a measurement. The switch was constructed from two small radio rheostats by mounting them on a common shaft and replacing their resistance windings with copper contacts.

Piezo-thermometric Cell.—The piezo-thermometric cell shown inside the cylindrical steel pressure bomb in Fig. 2 consisted of a soft-glass sphere 20 mm. in outside diameter with a gooseneck opening. It was held in place by a set of phosphor-bronze fingers shaped like a glassblower's flask-holder that were screwed to the recessed face of a cylindrical steel holder. This holder was sealed into the bomb by means of a threaded plug and a lead gasket.

The soldered junction of a copper–constantan thermocouple was at the center of the glass sphere and the wires[14] leading from it were fused through the rear wall. In order to get them out of the pressure bomb, they were fused into the end of a soft-glass capillary tube that previously had been cemented into a steel sheath with glycerol–litharge cement.[15] This sheath was sealed into an axial hole in the cylindrical steel cell holder by means of a packing of asbestos, shredded lead, and graphite.

When the cell was first constructed, the free ends of the thermocouple wires coming out of the open end of the glass capillary tube were drawn through a U-shaped copper conduit that was screwed on the end of the steel sheath. The wires were soldered to copper wires, and these junctions were enclosed in a glass tube that was cemented into the end of the copper conduit, thus forming a closed U-shaped thermocouple.

Before this thermocouple was calibrated it was pressure-seasoned by placing the cell in the bomb under a pressure of 50 bars for twenty hours at a temperature of 70°. Then the cell was subjected to twenty sudden applications and instantaneous releases of pressure of about 50 bars each.

The thermocouple was calibrated in a duplex thermostat by a direct differential method[16] in terms of a copper–constantan reference thermel, the calibration of which is described elsewhere.[16a] After calibration, the thermocouple wires were cut off just beyond where they emerged from the glass capillary tube, and new junctions to copper wires were made[17] and imbedded in paraffin in a thin-walled

---

(11) S. Kambara and M. Matsui, *J. Soc. Chem. Ind., Japan*, **34** (Suppl. binding), 94 (1931).

(12) Made by the Leeds and Northrup Company.

(13) W. P. White, THIS JOURNAL, **36**, 2011 (1914).

(14) Both wires were no. 40, B. & S. gage. The constantan wire had been selected to have a maximum inhomogeneity equivalent to 0.2% of its thermoelectric power against copper, after a test of a large quantity of wire by the method of W. P. White, *Phys. Rev.*, **31**, 135 (1910), p. 142.

(15) Contrary to the findings of H. Stäger, H. Zschokke and J. P. Bohnenblust [*Kolloid-Z.*, **65**, 319 (1933)] oil (Wyrol) attacked this cement at a temperature as low as 70°. To prevent this the bottom of the recess in the steel holder was covered with a zinc oxide–water glass emulsion, which set to a hard glaze that was not affected by Wyrol even at 110°.

(16) J. S. Burlew and R. P. Smith, THIS JOURNAL, **62**, 701 (1940). (a) This was Thermel B, p. 703.

(17) This operation did not affect the thermoelectric power of the thermel any more than the inevitable shift in the temperature gradient from its position during calibration to its position during use. Because this gradient had been kept unidirectional during calibration by the use of the duplex thermostat, the greatest change in the thermoelectric power caused by the shift of the gradient would have been 0.2%, which was the maximum measured inhomogeneity of the constantan wire. If the gradient during calibration had not

metal cylinder that can be seen screwed to the right end of the steel sheath in Fig. 2.

Two separate cells were constructed. The calibration of Cell A was performed in duplicate at mean temperatures of 20, 30, and 40°, with first one limb cold and then the other; but no systematic difference was observed between the two sets of results. Cell B was calibrated at mean temperatures of 5, 35, 65, 95, and 135°. Inasmuch as the differences in the thermoelectric power did not vary regularly with the mean temperature, the thermoelectric power of the thermocouple in each cell was expressed by the same function of the mean temperature t' as had been derived for the reference thermel, but with the constant term changed by the mean observed difference in thermoelectric power. For convenience in use over the limited temperature range 20 to 30°, the quadratic equation for Cell A was transformed into a linear form. The systematic probable error of the calibration equations is estimated to be ±0.1%, because of the uncertainty concerning the inhomogeneity of the constantan wire. The relative probable error of the equation for Cell A is ±0.03%, and of that for Cell B is ±0.15%, which combines the uncertainty of the original calibration of the reference thermel with the uncertainty of the comparison.

Technique

After the piezo-thermometric cell had been filled with the liquid to be studied, mercury was placed in the gooseneck until it came within 2 mm. of the entrance to the bulb. The bomb, containing the cell sealed in it, was filled with Wyrol[10] and the bomb-pipe was half-filled.[18] Pressure was applied to the cell by admitting nitrogen to the pressure distributor.[19] This always had to be done slowly in order to prevent mercury from being forced into the bulb of the cell. A preliminary measurement of $\Delta T/\Delta P$ was made, from which was computed the pressure drop needed to cause the thermocouple to develop a potential of between 15 and 16 μv. After this pressure had been applied, there was a wait of about an hour while the heat of compression leaked away.

When thermal equilibrium had been established within a few hundredths of a degree, the potentiometer dial was set at 15 μv., and the tapping key of the potentiometer was locked down. The release valve was opened suddenly, and at the same time the duplex switch (Fig. 3) was thrown from left to right. In the former position the battery had been connected to a by-pass resistance and the thermocouple had been connected to the galvanometer through the potentiometer coils and a damping resistance, so that the deflection of the galvanometer "spot" from its open-circuit position had been a measure of the temperature difference between the thermostat and the liquid in the cell. Turning the switch to the latter position applied the electromotive force of the potentiometer to the galvanometer. The thermocouple, however, had been cooled by the release of pressure; and since its potential opposed that of the potentiometer, the galvanometer. which first had moved toward its zero position while it was being short-circuited by the one moving arm of the duplex switch, finally was deflected a small amount. By a proper choice of the pressure drop this deflection was made to be always less than 2 cm. in the direction that indicated cooling of the liquid in the cell. The definiteness of the maximum of the galvanometer deflection was enhanced by the fact that the subsequent deflection, caused by the warming up of the cell to the temperature of the thermostat, was opposite the original deflection.

The position of the galvanometer spot before and after the release of pressure was estimated to the nearest 0.2 mm. The difference between the two positions measured[20] the amount by which the potential of the thermocouple exceeded the 15 μv. potential of the potentiometer. Thus the duplex switch not only obviated moving a contact in the galvanometer circuit at the time of a measurement, but also performed the same function as the eliminating switch[21] of a White potentiometer by furnishing a closed-circuit "zero."

As soon as the galvanometer spot began to drift, the duplex switch was placed in the short-circuiting position while pressure was reapplied. Thus the contents of the bomb were restored almost to thermal equilibrium with the thermostat. The potentiometer switch was thrown to the left, whereupon the galvanometer indicated that the cell was only about 0.1° warmer than the thermostat. This difference decreased in about five minutes to less than 0.02°. Ten minutes after the first release of pressure, a second measurement was made. This procedure was repeated for a total of five replicates. Then the temperature of the thermostat was raised, and the same routine was carried out at a new constant temperature.

The procedure of keeping the potentiometer setting the same for all measurements and varying the pressure, increased the precision considerably; for the pressure could be measured much more precisely than the electromotive force of the thermocouple. In effect the uncertainty of the adjustment of the potentiometer coils did not contribute to the observational error, but only to the systematic error. A similar increase in precision was obtained in connection with replicate measurements at a single temperature, by using the same pressure for all of them, so that the galvanometer deflection was the only quantity subject to significant observational variation. These two procedures had the important practical advantage that the mean temperatures for all observations of $(\Delta T/\Delta P)_S$ for a given liquid were a constant amount below the temperature of the thermostat, which simplified the mathematical reduction of the data.

---

been kept unidirectional, the possible change would have been much larger.

[18] The height of oil in the bomb-pipe increased from about 5 to 15 cm. during a series of experiments at different temperatures, because of the expansion of the oil in the bomb. The corresponding variation of the hydrostatic pressure on the cell, which amounted to ±5 millibars, was insignificant in view of the very small change of the temperature–pressure coefficient with pressure (*v. infra*).

[19] Although the application of pressure decreased the height of the oil column slightly, the decrease of the apparent pressure drop was less than 0.002%.

[20] During the course of a series of measurements the working sensitivity of the galvanometer, which varied gradually with change of room temperature, was measured at the beginning of each set of five measurements, by observing in duplicate the galvanometer deflection corresponding to a potential of 5 μv. Just prior to this observation the working current of the potentiometer was balanced against the standard cell.

[21] W. P. White, THIS JOURNAL, **36**, 1856 (1914), p. 1859.

TABLE I

VARIATION OF $(\partial T/\partial P)_S$ WITH PRESSURE

Toluene in Cell A Thermostat temperature: 26.00 ± 0.01°

Mean temp., °C.	ΔP, bars	ΔT, °C.	$10^2 \times (\Delta T/\Delta P)$, deg./bar	Mean pr., bars	$10^2 \times (\Delta T/\Delta P)$ cor. to 25.70°	$10^5 \Delta$	$10^2 \times (\partial T/\partial P)_S$ at 1 bar, 25.70°
25.49	47.536	1.0289	2.1646	24.3	2.1666	−1.3	2.189
25.55	42.026	0.9104	2.1664	21.5	2.1678	+0.2	2.188
25.61	35.825	.7781	2.1720	18.4	2.1728	−1.8	2.190
25.67	30.313	.6579	2.1703	15.7	2.1706	+3.0	2.185
25.74[a]	24.114	.5246	2.1756	12.6	2.1754	+1.1	2.187
25.74[a]	24.114	.5247	2.1760				
25.80	17.912	.3920	2.1882[b]	9.5	2.1874	....	2.196
25.86	12.400	.2710	2.1852	6.7	2.1837	−1.5	2.189

[a] These two series of determinations were performed on two different days. Their mean was used as a single point in the least squares computation. [b] This value, which was in considerable disagreement with all the others, was neglected in the derivation of the equation.

Experimental Study of Method

Time between Successive Observations.—As the result of one hundred systematic observations of $(\Delta T/\Delta P)$ it was found that when the time between successive observations was six minutes or less the apparent cooling of the liquid was about 0.1% less than when a longer period elapsed, probably because of lack of thermal equilibrium in the cell. Hence it was concluded that the time between successive observations should be not less than ten minutes; and this rule was followed in all subsequent experiments.

Decrease of $(\partial T/\partial P)_S$ with Pressure.—The adiabatic temperature–pressure coefficient of a liquid decreases with increase of pressure, as was demonstrated by Pushin and Grebenshchikov[22] in the case of a number of organic liquids at pressures of 500 to 3000 bars. An extrapolation of their data for benzene at 90° to the relatively low pressure of 10 bars gives −0.059% per bar for the variation with pressure of $(\partial T/\partial P)_S$. Richards and Wallace[6] found no variation with pressure of $(\partial T/\partial P)_S$ over a range of mean pressures from 8 to 13 bars, probably because the error of an individual measurement was great enough to obscure the variation with pressure over such a small range of pressure.

In the present investigation the pressure variation of $(\partial T/\partial P)_S$ of toluene was measured. Eight sets of five observations each were made with the thermostat at 26.00°, using pressure differences of 12 to 47 bars, as shown in Table I. Not only was the range of mean pressures three times as great as that used by Richards and Wallace; but also the precision of the result was increased by making replicate observations at identically the same mean pressure, instead of using a different pressure for each observation, as they had done.

Because the amount of cooling of the liquid varied with the pressure difference, the mean temperature of the liquid varied by 0.4°. Before the results at different pressures could be compared, they had to be corrected to the same mean temperature, for which 25.70° was chosen, because it was in the middle of the range. The correction of $(\Delta T/\Delta P)$ to 25.70° was made in accordance with the linear temperature variation that was determined for this same sample in the same cell by measurements at 20, 22, 24, 26, 28 and 30°. These corrected values of $(\Delta T/\Delta P)$, which are listed in the sixth column of Table I, were fitted by the method of least squares to a linear equation in which the mean pressure was the independent variable, with this result:

$$(\Delta T/\Delta P) = 2.1877 \times 10^{-2} - 9.6 \times 10^{-6}(P - 1) \quad (2)$$

from which it follows that $(\partial T/\partial P)_S$ decreased 0.044 ± 0.005% per bar of mean pressure. The residuals with respect to this equation are given in the next to the last column of Table I. The probable error of a single observation of $(\Delta T/\Delta P)$ computed from these residuals is $\pm 1.4 \times 10^{-5}$. The last column of Table I lists the values of $(\partial T/\partial P)_S$ corrected to atmospheric pressure (1 bar) and the temperature 25.70°, from which it will be seen that the variation that had characterized the original values of $(\Delta T/\Delta P)$ in the fourth column has been reduced considerably by the correction to a uniform temperature and pressure.

Effect of Medium Surrounding the Cell.—The time required for the center of a sphere of liquid to begin to warm up following a sudden release of pressure will be shorter the smaller the radius of the sphere and the larger the thermal

---

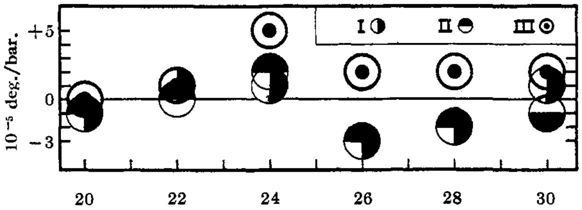
[22] N. A. Pushin and E. V. Grebenshchikov, *J. Chem. Soc.*, **125**, 2043 (1924).

head between the liquid and the enveloping sphere. Although the glass wall of the thermometric cell furnished the maximum thermal head, because its temperature–pressure coefficient was only about 5% as large as that of the Wyrol that surrounded it, the Wyrol did act as a reservoir of heat after an expansion. When toluene was in the cell, for instance, the thermal head glass-to-toluene was 50% greater than the thermal head glass-to-Wyrol. Therefore it was considered possible that with a sphere as small as that used, the excess heat in the Wyrol might have been great enough so that the temperature at the center of the cell would have begun to change before it was measured.[23]

This possibility was investigated experimentally. Three series of measurements were made with portions of the same sample of toluene in Cell A at 2° intervals from 20 to 30°. Series I and II were performed a week apart with Wyrol in the bomb surrounding the cell. Series III was performed two days before Series II with toluene instead of Wyrol in the bomb. The following linear equation was derived by the method of least squares from the combined results of Series I and II:

$$(\partial T/\partial P)_S = 2.1835 \times 10^{-2} + 9.08 \times 10^{-5}(t' - 25) \quad (3)$$

The residuals with respect to this equation are shown in Fig. 4, from which it will be seen that the temperature decrease measured when toluene surrounded the cell was a trifle less than that measured when Wyrol surrounded the cell. This difference, which was just about the experimental uncertainty, was opposite that expected if the medium surrounding the cell had affected the measured temperature difference. Hence it was concluded that the use of Wyrol as the pressure-transmitting liquid introduced no error.



Centigrade temperature.

Fig. 4.—Residuals of $(\partial T/\partial P)_S$.

Contamination by Wyrol.—The data in Fig. 4 indicate that the mercury in the gooseneck of the cell acted as a complete barrier to the entrance of Wyrol. The measurements at 30° with Wyrol in the bomb gave results slightly higher than those with toluene in the bomb; whereas if a little Wyrol had slipped past the mercury during the previous twenty-five applications and releases of pressure, it would have lowered $(\partial T/\partial P)_S$.

Precision and Accuracy.—The *a priori* estimates of the probable errors involved in the measurement of the temperature–pressure coefficient of a liquid with the apparatus that has been described are summarized in Table II, which lists the effect on $(\partial T/\partial P)_S$ from each such error.

The data presented in Fig. 4 for $(\partial T/\partial P)_S$ of toluene measured on different days with the same cell illustrate the validity of these estimates of the total observational errors at a single temperature. The root mean square deviation of each value of $(\partial T/\partial P)_S$ from the mean of a pair of duplicates on different days was ±0.02%; the estimate given in Table II is ±0.06%.

TABLE II

ESTIMATED PROBABLE ERROR OF $(\partial T/\partial P)_S$

Observed quantity	Errors, % Observational	Systematic
1. Pressure difference		
a. Gage weights	±0.001	±0.001
b. Piston area	.....	± .05
c. Height of oil in gage	± .005	.....
d. Temperature of gage	± .005	.....
2. Electromotive force		
a. Potentiometer coils	.....	± .07
b. Battery current	± .01	.....
c. Galvanometer deflection (for mean of five replicates)	± .05	.....
3. Thermoelectric power of thermel	.....	± .18
4. Temperature of thermostat	± .015	.....
5. Pressure correction[a]	.....	± .05
Total	±0.06	±0.21

[a] See p. 688 for a discussion of the uncertainty of the pressure correction at higher temperatures.

Confirmation of the estimates of the other errors, including some of the systematic ones, was sought by making measurements with the same sample of liquid in two different individually calibrated cells at 2° intervals from 20 to 30°. All the values of $(\partial T/\partial P)_S$ both of benzene and of toluene obtained with Cell A were less than those obtained with Cell B. The root mean square deviation of each individual value from the mean

---

(23) Dr. William T. Richards has suggested in a private communication that the effect of radiation on the thermocouple was negligibly small. His opinion is supported by a calculation based on Kirchoff's law and the Stefan–Boltzmann law, which shows that the thermocouple would have been heated less than 0.0001°, if it is assumed that (a) the liquid in the cell transmitted only 0.1% of the black body radiation corresponding to temperatures below 110° and (b) the thermocouple junction absorbed 50% of the radiation incident upon it.

of a pair of duplicates was ±0.10% for benzene and ±0.22% for toluene; whereas the combined value of the estimates of both the observational and systematic probable errors in Table II is ±0.22%.

Samples

Distillation Apparatus.—As the final step in its purification each sample was distilled in an all-glass apparatus that had interchangeable distilling flasks and interchangeable receivers. The round distilling flasks used were of different diameters, but each had a straight tube 3 cm. long and 1.5 cm. in diameter sealed on the bottom. An electric heater was wound on a copper tube that fitted snugly over this extension. Thus boiling took place in this small space, which had a volume of only 6 ml. An inverted cone of sheet copper resting on the upper surface of the distilling flask prevented excessive condensation there. The vacuum-jacketed column, 60 cm. high, which was packed with one-turn glass helices,[24] was surmounted by a reflux condenser. The progress of a distillation was followed by measurement of the refractive index of successive small fractions with an Abbé refractometer. The absolute accuracy of the refractive indices was not known, but the relative precision was ±0.0001.

Benzene.—Some Merck "reagent grade benzene, thiophene-free" was purified by treatment with the following reagents in succession: concentrated sulfuric acid, water, a dilute solution of sodium hydroxide, water, calcium chloride, hot mercury, and phosphorus pentoxide. Then it was fractionated. The refractive index was raised 0.0003 by the purification.

Toluene A.—Sample A, which was purified only slightly in order to give a basis of comparison for the highly purified Samples B and C, was obtained by distillation of 120 ml. of C. P. toluene from the General Chemical Company. After 50 ml. had passed over, a fraction of 6 ml. was preserved. Its refractive index was 0.0007 higher than that of the original material, but 0.0008 lower than that of Samples B and C.

Toluene B.—Some Baker C. P. toluene was purified by treatment with the following reagents in succession: hot mercury, concentrated sulfuric acid, water, a dilute solution of sodium hydroxide, water, calcium chloride, and phosphorus pentoxide. After fractionation, it was refluxed over sodium for two hours, and then fractionated from it. The refractive index was unchanged by this last distillation.

Toluene C.—Some Merck "reagent grade toluene" was purified principally by the preparation of toluenesulfonic acid,[25] from which the toluene was regenerated by distillation with superheated steam. It was treated further with concentrated sulfuric acid, water, a dilute solution of sodium hydroxide, water, and calcium chloride in turn. After having been refluxed over sodium for two hours, it was fractionated from the sodium. A forerun of 3 ml. was discarded, and the other fractions were mixed and refluxed over fresh sodium for an hour, after which the final sample was distilled off in several fractions, all of which had the same refractive index, which was only 0.0001 higher than that of the starting material. It was the same as the index of Sample B.

Effect of Impurities on $(\partial T/\partial P)_S$.—Six series of measurements, consisting of five replicates each, were made at 2° intervals from 20 to 30° with each sample of toluene in Cell A. The mean value for each sample, which was $(\partial T/\partial P)_S$ at 25°, was $(2.1808 \pm 0.0014) \times 10^{-2}$ deg./bar for Sample A, $(2.1827 \pm 0.0007) \times 10^{-2}$ for B, and $(2.1830 \pm 0.0004) \times 10^{-2}$ for C. In other words, Samples B and C were indistinguishable as far as $(\partial T/\partial P)_S$ was concerned although $(\partial T/\partial P)_S$ for the slightly impure sample was 0.1% lower than for the pure ones.

Experimental Data

Definitive measurements of $(\partial T/\partial P)_S$ of benzene and of toluene (Sample C) were made with Cell B at 3° intervals from 8° to the respective b. p., with the results shown in Tables III and IV: where t', the mean temperature of the liquid during an expansion, equals the thermostat temperature minus $\Delta T/2$; ΔP is the instantaneous pressure drop; and ΔT is the accompanying decrease of temperature.

TABLE III

MEASUREMENTS OF TEMPERATURE–PRESSURE COEFFICIENT OF BENZENE

t', °C.	ΔP, bars	ΔT, °C.	$10^2 \times (\Delta T/\Delta P)$, deg./bar	$10^2 \times (\partial T/\partial P)_S$, deg./bar	$10^6 \times \Delta^a$
7.80	18.604	0.40927	2.1999	2.2080	+24
10.79	18.604	.41551	2.2334	2.2417	+ 9
13.79	18.604	.42209	2.2688	2.2773	−22
16.79	17.914	.41182	2.2989	2.3072	+ 5
19.79	17.912	.41726	2.3295	2.3379	+27
22.80	17.223	.40754	2.3663	2.3744	− 6
25.79	17.224	.41341	2.4002	2.4084	−11
28.80	16.534	.40216	2.4323	2.4402	+10
31.80	16.534	.40824	2.4691	2.4772	−17
34.80	15.845	.39683	2.5044	2.5122	−19
37.81	15.155	.38467	2.5382	2.5457	− 1
40.80	15.155	.39093	2.5795	2.5872	−57
43.80	15.155	.39579	2.6116	2.6194	−14
46.81	14.465	.38317	2.6489	2.6563	−11
49.81	14.465	.38838	2.6850	2.6925	+ 6
52.81	13.774	.37460	2.7196	2.7268	+49
55.81	13.774	.37999	2.7587	2.7660	+51
58.81	13.774	.38644	2.8056	2.8130	−17
61.81	13.087	.37268	2.8477	2.8548	−24
64.81	13.087	.37906	2.8965	2.9038	−93
67.84	12.399	.36224	2.9215	2.9281	+94
70.82	12.400	.36816	2.9690	2.9759	+56
73.81	12.400	.37405	3.0165	3.0236	+30
76.82	11.712	.35892	3.0645	3.0712	+16
79.82	11.712	.36562	3.1218	3.1286	−85

[a] Δ = *calcd.* minus *exptl.*

Each value of the apparent temperature–pressure coefficient $(\Delta T/\Delta P)$ was corrected to a mean

---

[24] C. D. Wilson, G. T. Parker and K. C. Laughlin, THIS JOURNAL, **55**, 2795 (1933); E. E. Roper, G. F. Wright, J. R. Ruhoff and W. R. Smith, *ibid.*, **57**, 954 (1935).

[25] A. F. Holleman and P. Caland, *Ber.*, **44**, 2504 (1911).

TABLE IV

MEASUREMENTS OF TEMPERATURE–PRESSURE COEFFICIENT OF TOLUENE

t', °C.	ΔP, bars	ΔT, °C.	$10^2 \times (\Delta T/\Delta P)$, deg./bar	$10^2 \times (\partial T/\partial P)_S$, deg./bar	$10^6 \times \Delta^a$
7.79	20.668	0.41892	2.0269	2.0355	+ 9
10.79	19.980	.41002	2.0522	2.0605	+21
13.79	19.981	.41563	2.0801	2.0885	+ 5
16.80	19.291	.40616	2.1054	2.1135	+21
19.80	18.605	.39637	2.1304	2.1383	+41
22.80	18.604	.40183	2.1599	2.1679	+15
25.80	18.601	.40690	2.1875	2.1956	+11
28.80	17.911	.39749	2.2193	2.2272	−29
31.80	17.911	.40188	2.2438	2.2518	+ 4
34.80	17.224	.39151	2.2730	2.2807	− 2
37.80	17.224	.39706	2.3053	2.3131	−38
40.81	16.534	.38624	2.3360	2.3435	−50
43.80	16.534	.39109	2.3654	2.3731	−50
46.80	15.845	.38000	2.3982	2.4057	−73
49.81	15.844	.38348	2.4203	2.4278	+13
52.81	15.155	.37174	2.4529	2.4601	+ 4
55.81	15.155	.37718	2.4888	2.4961	−36
58.81	15.155	.38168	2.5185	2.5259	− 7
61.82	14.467	.36917	2.5518	2.5588	− 2
64.81	14.467	.37428	2.5871	2.5943	−16
67.81	14.467	.37838	2.6155	2.6228	+48
70.82	13.776	.36560	2.6539	2.6608	+26
73.82	13.776	.37090	2.6924	2.6994	+ 6
76.82	13.088	.35660	2.7246	2.7313	+61
79.80	13.087	.36193	2.7656	2.7726	+32
82.77	13.087	.36701	2.8044	2.8118	+34
85.76	12.400	.35303	2.8470	2.8542	+13
88.80	12.400	.35870	2.8927	2.8996	−27
91.81	12.400	.36334	2.9302	2.9371	+23
94.78	11.712	.34861	2.9765	2.9834	− 5
97.82	11.712	.35385	3.0213	3.0279	− 3
100.83	11.712	.35911	3.0662	3.0728	+ 7
103.83	11.023	.34342	3.1155	3.1217	−11
106.81	11.023	.34865	3.1629	3.1394	− 5
109.83	11.023	.35450	3.2160	3.2225	−40

[a] Δ = *calcd.* minus *exptl.*

pressure of 1 bar by means of the pressure coefficient −0.044% per bar that had been found[26] for toluene at 25.7°. This same coefficient was used to correct the measurements at all temperatures, for the pressure variation of $(\partial T/\partial P)_S$ was not measured at other temperatures because of lack of time. A change with temperature of ±50% in the pressure variation would cause an error of only ±0.2% in $(\partial T/\partial P)_S$. It is assumed[27] also that within these limits the same correction applies to benzene. When the mean temperature differed by a few hundredths of a degree from a value of 0.20° less than a whole degree, a correction amounting to 1×10^{-6} deg./bar for each hundredth of a degree was applied to $(\Delta T/\Delta P)$, so that the corrected values of $(\partial T/\partial P)_S$ in the fifth column refer to a mean pressure of 1 bar and a mean temperature 0.20° less than the whole degree next higher than that shown in the first column.

$(\partial T/\partial P)_S$ as a Function of Temperature.—Search for a suitable temperature function was made by analysis of the data for toluene by means of first, second, and third differences according to the plan outlined by Running.[28] Twelve three-parameter functions were tested by evaluating their parameters at the end and middle points and then computing two intermediate points. A cubic equation without a quadratic term and a double logarithmic equation involving the absolute temperature were the only ones that were very promising. These two together with the full cubic equation (four parameters) were investigated more carefully by evaluating their parameters by the method of least squares, using all the points. The probable error of an individual observation based on the residuals did not vary more than 10% for these three equations. The double logarithmic equation was discarded, however, because of a pronounced trend in the signs of the residuals. The data for benzene also were fitted to three- and four-parameter cubic equations by the method of least squares. The probable error of an individual observation was the same for both equations. Therefore, since the three-parameter cubic equation gave as good a general representation of the data for $(\partial T/\partial P)_S$ of both benzene and toluene as did the four-parameter cubic, it was preferred in the interest of simplicity.

---

(26) *Cf.* eq. (2).

(27) This assumption is substantiated partially by a calculation of $d(\partial T/\partial P)_S/dP$ that is made possible by the recently published data of R. E. Gibson and J. F. Kincaid [THIS JOURNAL, **60**, 511 (1938)] for the variation with pressure of the coefficient of thermal expansion of benzene. From the parameters in the equations for the coefficient of thermal expansion at five different pressures from 1 to 1000 bars, given in their Table V, the value of $d(\partial V/\partial T)_P/dP$ has been computed to be -8.6×10^{-7} (cc./g.-deg.)/bar at 25° and a mean pressure of 10 bars. The pressure variation of $(\partial T/\partial P)_S$ has been computed by means of this equation

$$\left[\frac{\mathrm{d}}{\mathrm{d}P}\left(\frac{\partial T}{\partial P}\right)_S\right]_T = \frac{T}{(c_\mathrm{p})^2}\left\{c_\mathrm{p}\left[\frac{\mathrm{d}}{\mathrm{d}P}\left(\frac{\partial V}{\partial T}\right)_P\right]_T - \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial c_\mathrm{p}}{\partial P}\right)_T\right\} \tag{4}$$

using data from the present investigation for the other terms. At 25° $d(\partial T/\partial P)_S/dP$ is −0.054 ± 0.006% per bar. At higher temperatures the computed value increases numerically to −0.084% at 80°; but inasmuch as this temperature slope is due to a similar slope in $d(\partial V/\partial T)_P/dP$, and inasmuch as this slope was derived from a quadratic equation passed through four points based on measurements at a maximum temperature of 65°, the increase of $d(\partial T/\partial P)_S/dP$ may have been exaggerated.

(28) T. R. Running, "Empirical Formulas," John Wiley and Sons, Inc., New York, N. Y., 1917.

The equations evaluated by least squares were:

$$[C_6H_6]\ (\partial T/\partial P)_S = 2.12695 \times 10^{-2} + 1.06806 \times 10^{-5}t + 2.7715 \times 10^{-9}t^3 \quad (5)$$

$$[C_7H_8]\ (\partial T/\partial P)_S = 1.96840 \times 10^{-2} + 8.6990 \times 10^{-5}t + 2.2285 \times 10^{-9}t^3 \quad (6)$$

The residuals with respect to these equations are listed in the last column of Tables III and IV, respectively. The probable error of an individual observation based on the residuals was ±2.9 × 10^{-5} and ±2.0 × 10^{-5}, respectively. These values are less than twice as great as the *a priori* estimates of the total observational probable error given in Table II. Values of $(\partial T/\partial P)_S$ for benzene and toluene computed at 5° intervals from equations (5) and (6) are listed in Table II of the paper[8] on the heat capacity of these liquids.

Comparison of Data.—A comparison of the present data with those of Richards and Wallace[6,29] is given in Table V. The differences between the two sets of data are actually larger than they appear at first, because the present values have been raised 7 × 10^{-5} on the average by the correction to 1 bar and also because the values of Richards and Wallace refer to the temperature of the thermostat rather than to the mean temperature of the liquid during the expansion. Inasmuch as the liquid cooled during the expansion, the value of $(\partial T/\partial P)_S$ that they reported for a particular temperature is a little too small. If we may judge from the data for benzene at 40° in their Table I, $(\partial T/\partial P)_S$ should be raised 3 × 10^{-5}. For the purpose of computing the deviations between the two sets of data, given in Table V, the values of Richards and Wallace have been increased by 1 × 10^{-4}. Except for the results at 20°, the agreement is fairly satisfactory.

TABLE V

COMPARISON OF DATA FOR $(\partial T/\partial P)_S$ WITH RESULTS OF RICHARDS AND WALLACE

$10^2 \times (\partial T/\partial P)_S$ in deg./bar

	Benzene			Toluene		
t, °C.	Burlew	R. & W.	Dev.,[a] %	Burlew	R. & W.	Dev.,[a] %
20	2.343	2.365	+1.4	2.144	2.162	+1.3
30	2.455	2.470	+1.0	2.235	2.242	+0.8
40	2.572	2.583	+0.8	2.331	2.334	+ .6
50	2.696	2.696	+ .4	2.431	2.438	+ .7

[a] Dev. = (*R. & W.* plus 1 × 10^{-4}) minus *Burlew* (see text).

Acknowledgments.—It is a pleasure to acknowledge the encouragement and advice given by Professor Donald H. Andrews during the course of this research. I thank Professor Herbert S. Harned and the other members of the staff of the Department of Chemistry at Yale University for their kindness in making available facilities for research. I am indebted to Mr. H. S. Bittner and Mr. Harry Johns of the Chemistry Shop, Johns Hopkins University, and to Mr. J. M. Berney, Mr. H. G. Cady, Mr. Wm. Duncan and Mr. F. P. Noble of the Chemistry Shop, Yale University, for the interest they took in the careful fabrication of the apparatus.

Summary

An apparatus has been described for the measurement of $(\partial T/\partial P)_S$ of 5 ml. of a liquid, the precision of the observations has been discussed, and the use of the apparatus has been illustrated by data for benzene and toluene at 3° intervals from 8° to the respective boiling points.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 21, 1939

---

[29] Their original values have been changed from the unit "deg./atm." to "deg./bar" by multiplication by the factor 0.98692 atm./bar.