[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Measurement of the Heat Capacity of a Small Volume of Liquid by the Piezo-thermometric Method. II. Coefficient of Thermal Expansion of Benzene and of Toluene Measured with a New Type of Weight Dilatometer

BY JOHN S. BURLEW[1]

In the application of the piezo-thermometric method[2] to the measurement of the heat capacity of a sample of liquid as small as 5 cc., it is necessary to have a means of measuring the coefficient of thermal expansion of this quantity of liquid with a probable error of not more than ±0.3% over a wide range of temperature, without regard to the volatility of the liquid. The weight dilatometer (Fig. 1) devised for the purpose is similar in design to the Meyer–Neubeck pycnometer,[3a] except that in the present dilatometer a fixed weight of liquid is confined by mercury, so that the instrument may be used at any temperature up to the temperature of the boiling point.

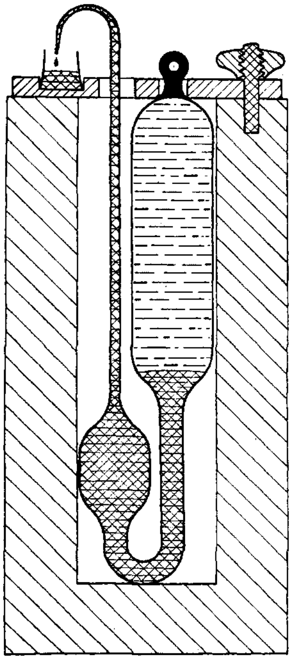

Fig. 1.—Weight dilatometer in steel holder (scale, 2/3).

The principle of this weight dilatometer is that the volume of liquid present at a given temperature can be computed from the weight of mercury contained at a reference temperature and the amount expelled when the dilatometer is heated to the given temperature, the volume of liquid present at the reference temperature being known. The total volume of the dilatometer at any temperature is equal to the sum of the volume of the liquid and the volume of mercury. Expansion of this fundamental relation in terms of the quantities actually measured gives the following equation[4] for the specific volume

$$v_t = \frac{1}{w}\left\{ V_\Theta\,[1 + a(t - \Theta)] - \frac{w'_\Theta - w^*_t}{d'_t} \right\} \qquad (1)$$

Dilatometers employing this same principle have been described by Pesce and Hölemann[5] and by Jones and Jelen.[6] Each of them was larger and more elaborate, but furnished results no more precise. The present instrument recently has been adapted[7] to use with solutions.

Weight Dilatometer

Holder.—The dilatometer fitted into a circular hole drilled in a steel cylinder, as shown in Fig. 1. A circular cover plate screwed to the top of the cylinder kept the dilatometer submerged in the mercury with which the hole was filled. The glass ring at the rounded end of the dilatometer projected through a hole in the cover plate, and the capillary neck emerged through a notch cut in its side. The main portion of the dilatometer, which had been blown from 15-mm. pyrex glass tubing, had a volume of 3.5 cc.; the smaller tube and capillary 0.5 cc.; and the bulb 1 cc. The orifice at the end of the capillary neck was less than 0.1 mm. in diameter. A glass cup (6 by 7 mm.) that rested in a small recess cut in the cover plate,[8] caught the overflow of mercury from the capillary neck when the temperature was raised.

Thermostat.—A region of uniform temperature for the dilatometer was provided by an aneroid thermostat:

---

[1] Sterling Fellow, 1934–1936; present address: Geophysical Laboratory, Washington, D. C.

[2] See paper I of this series, THIS JOURNAL, **62**, 681 (1940).

[3] F. Neubeck, *Z. physik. Chem.*, **1**, 649 (1887); (a) p. 652; (b) pp. 654 and 656.

[4] The symbols used in this paper are as follows: v_t is the specific volume of the liquid under investigation; V_t is the total volume of the dilatometer; V'_t is the volume of mercury in the dilatometer; W_t is the total weight of the contents of the dilatometer; w is the constant weight of liquid in the dilatometer; w'_t is the weight of mercury in the dilatometer; w^*_t is the weight of mercury expelled between a temperature t and the next lower temperature at which an observation was made; d_t is the density of the liquid; d'_t is the density of mercury; and a is the coefficient of thermal expansion of the dilatometer. The subscript t refers to any temperature and the subscript Θ refers to an arbitrary reference temperature.

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

[6] G. Jones and F. C. Jelen, THIS JOURNAL, **57**, 2532 (1935).

[7] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **61**, 2515 (1939).

[8] Figure 1 shows the dilatometer as if it had been rotated through an angle of 90° with respect to the diameter of the cover plate passing through the cup and the wing nut.

a brass cylinder that stood on three legs on the bottom of an oil thermostat. To the top of this cylinder, which was 7 cm. in diameter and 12 cm. high, was soldered a cylindrical extension about 20 cm. long, made from sheet copper, the upper end of which reached just above the surface of the oil. The steel holder for the dilatometer fitted snugly into an axial hole in the brass cylinder. It was raised and lowered by a stiff wire handle that was screwed into its top. The upper end of the aneroid thermostat was closed with a cork. In this way it was not necessary to make any correction for the small length of capillary that was not immersed in the mercury in the holder, for it was at substantially the same temperature as the immersed part.

Filling.—The dilatometer was filled by suction in a test-tube (4 by 18 cm.) provided with two side-arms carrying stopcocks. One was connected to an aspirator or vacuum pump and the other to a calcium chloride tube open to the air. First the dilatometer was hung by its capillary neck from a small cup filled with mercury. By evacuating the tube and then admitting dry air, mercury was forced into the dilatometer.

The dilatometer was turned upside down, and the mercury was shaken into the main portion of the instrument. A sample of the liquid to be studied, freshly boiled and then cooled to about 50° below its boiling point, was placed in a glass cup that rested on the bottom of the filling tube, and the capillary neck of the inverted dilatometer was submerged in it. The liquid was placed in the cup instead of directly in the filling tube in order to decrease the volume needed. The filling tube was evacuated until the liquid began to boil, when evacuation was stopped. Air was admitted slowly to the filling tube, whereupon the liquid rushed into the dilatometer. The lower end of the filling tube was cooled with ice water, so that when the tube was evacuated a second time the last traces of air were removed from the dilatometer by the boiling of the warm liquid in it, without boiling the liquid that remained in the filling cup. When air was readmitted to the filling tube, liquid completely filled the dilatometer, except for a tiny bubble at the top of the bend. This bubble was removed through the capillary stem by gently warming the instrument until a small quantity of mercury had been expelled. The capillary tube was dried on the inside by alternately cooling and heating the dilatometer half a dozen times.

Determination of w.—The dilatometer next was filled completely at a convenient reference temperature (t_Θ) near room temperature. It was placed in warm water until mercury began to be expelled, after which it was cooled to slightly below t_Θ while the nose of the capillary was held under the surface of mercury. Then it was placed in its steel holder in the aneroid thermostat at t_Θ for at least forty minutes; the steel holder previously had been in the thermostat at t_Θ. From the weight of the dilatometer after having been filled at t_Θ in this manner, the amounts of mercury and of liquid contained were computed by means of equations (3) below.

It is possible to measure w and w'_Θ directly at the time of filling the dilatometer (this was done during the calibration), but during routine measurements it is preferable to derive them from the total weight (W_Θ) of the contents of the dilatometer and the total volume (V_Θ). This procedure permits the use of a permanent table of volumes of the dilatometer, and also it does away with one tedious step in the filling of the instrument—namely, catching and weighing the mercury that is expelled when the final air bubble is being removed. The indirect determination of w and of w'_Θ is based on the simultaneous solution of two equations

$$W_\Theta = w + w'_\Theta = (V - V')_\Theta\, d_\Theta + (V'd')_\Theta \quad (2)$$

which gives

$$w = \left\{\left(\frac{d}{d' - d}\right)_\Theta\right\}\left\{(Vd')_\Theta - W_\Theta\right\} \quad (3a)$$

$$w'_\Theta = W_\Theta - w \quad (3b)$$

In one filling of the dilatometer with benzene, w was determined both directly and indirectly, with a difference of 0.4 mg. between the two values, which is good agreement, inasmuch as the direct determination involved four weighings for each of which the probable error was ±0.1 mg.

Measurements.—Although measurements at different temperatures could be made in any order desired, it was convenient to start a series of them with the weight dilatometer at 0° if possible. The dilatometer was filled at 0° by being packed in ice with its nose in a cup of mercury. Handling of the instrument during its transfer to the thermostat that had been set at the next higher temperature was facilitated by chilling it below 0° by pouring strong brine over the ice. After the dilatometer had been in the aneroid thermostat at a constant temperature for one hour, with a receiving cup under the end of the capillary tip, the cup was replaced by an empty one, and the temperature of the thermostat was raised to the next higher temperature; and so on.

Calibration.—The weight dilatometer was calibrated by means of a series of measurements with water at 10° intervals from 10 to 90°. The weight of mercury and water contained at 30° was determined separately, and then the mercury expelled during the successive heating periods was weighed. The specific volume of mercury was computed by the following formula given by Scheel and Blankenstein[9]

$$1/d'_t = 0.0735560(1 + 1.8182 \times 10^{-4}t + 7.8 \times 10^{-9}t^2)\ \text{cm.}^3/\text{g.} \quad (5)$$

The density of water in g./cc. was computed from the density in g./ml. listed in the "Int. Crit. Tables."[10] The values for the volume of the dilatometer at different temperatures, computed according to eq. (1), were fitted to a linear equation in t by the method of least squares, with this result

$$V_t(\text{cm.}^3) = 5.29379 + 5.625 \times 10^{-5}t \quad (6)$$

The relative probable error of V_t based on the residuals with respect to this equation was $\pm 2 \times 10^{-5}$ at the ends of the range, and only $\pm 0.8 \times 10^{-5}$ in the middle. The systematic probable error, however, was $\pm 3 \times 10^{-4}$, because of the uncertainty in the weight of water contained.

The coefficient of thermal expansion of the pyrex glass of the dilatometer as determined by this calibration was $1.063 \pm 0.005 \times 10^{-5}$. This value differs by 7.8% from that of 0.985×10^{-5} reported by Jones and Jelen[6] for their dilatometer; but the difference is not surprising

---

(9) K. Scheel and F. Blankenstein, *Z. Physik*, **31**, 202 (1925).

(10) "Int. Crit. Tables," Vol. III, pp. 25-26.

in view of the different heat treatments of the two instruments.

Precision and Accuracy

Systematic tests demonstrated that the dilatometer, if left in the thermostat for at least thirty minutes, could be filled at a particular temperature with an error not greater than the error of weighing, namely, ±0.1 mg.

The question of whether the mercury used as a confining liquid had the same density and coefficient of expansion as that used by Scheel and Blankenstein did not affect the accuracy of the specific volume measurements made with the weight dilatometer, because about the same quantity of the same mercury was used during both the calibration and the volume measurements.

The systematic probable error for the present dilatometer (caused by the uncertainty in the weight of liquid contained compared with the weight of water contained during the calibration) was ±0.01%. This uncertainty, which limits the accuracy of the measurements of specific volume, does not affect their relative precision; hence its effect on the accuracy of the coefficient of thermal expansion is negligible.

The maximum relative probable error of the total volume (caused by the uncertainty in the coefficient of expansion of the dilatometer) was $\pm 2 \times 10^{-5}$ cc., and that of the volume of mercury at any particular temperature (caused by the uncertainty[11] in the weight of mercury contained at different temperatures) was $\pm 4 \times 10^{-5}$ cc. Inasmuch as it is the difference of these two volumes that is proportional to the specific volume of liquid, the relative probable error of the latter was $\pm 6/w \times 10^{-5}$ cc./g., which became ±0.0017%, when w, the weight of liquid contained, was 3.5 g.

The fourth source of error was the uncertainty in the temperature observations. Its contribution[12] to the total uncertainty in the specific volume is proportional both to the probable error of the temperature and to the coefficient of thermal expansion.

Combination of the errors from these four sources yields the following *a priori* estimates of the total probable error of the specific volume in the middle of the range: $\pm 3.5 \times 10^{-5}$ cc./g.-deg. for benzene and $\pm 4.4 \times 10^{-5}$ cc./g.-deg. for toluene.

The functional relation between the specific volume and the temperature should be derived by the method of least squares under the condition[13] that both these variables are subject to error. The labor of computation may be reduced considerably without violating this condition, if the observations are arranged to be made at equal intervals of temperature and with the probable errors approximately the same (say within a factor of two) for all points. Then the equation can be evaluated from the points distributed symmetrically on each side of the mid-point of temperature, each point being considered of unit weight.

Influence of Number of Observations

The relation of the probable error of the coefficient of thermal expansion to the probable error of the specific volume of a liquid depends considerably on the number of values of the specific volume at different temperatures and on their distribution. In order to find out how many observations with the weight dilatometer were needed to furnish a reliable value of the expansion, the proportional probable error of the coefficient of thermal expansion was computed[14] for different values of n, the number of observations, and of x, the independent variable. The results are given in Table I. Each curve of specific volume was assumed to have its points distributed symmetrically on either side of the mid-point ($x = 0$) from $x = -(n - 1)/2$ to $+(n - 1)/2$ and was assumed to be represented by a cubic equation.

From Table I it may be seen that over more than half the range of a cubic curve the probable error of the slope is not greater than it is at the mid-point, whereas at the ends of the range it is regularly nearly four times as large. Hence the probable error of the slope at the mid-point, which is very easy to compute, is a useful indicator of the reliability of the slope throughout the course of the curve.

---

[11] The errors of weighing the separate portions of mercury expelled, which are cumulative, can be minimized by weighing the dilatometer after it has been at the maximum temperature and then adjusting the individual values of w^*. When this is done the probable error in a single value of $(w'_\Theta - w^*_t)$ does not exceed ±0.5 mg., which is equivalent to an uncertainty of $\pm 4 \times 10^{-5}$ cc. in the volume.

[12] For a liquid with an expansion of 0.001 cc./g.-deg. this contribution is 0.001% for a temperature uncertainty of 0.01°. Hence a weight dilatometer of the dimensions given above is sufficiently precise to make it worthwhile to employ a thermometer having a relative probable error of ±0.005° for measurements with organic liquids having coefficients of thermal expansion about 0.0015. In that case the total uncertainty in the specific volume would be a little less than $\pm 2 \times 10^{-5}$ cc./g.-deg. In order to reduce it to one-half this amount, the dilatometer would have to be enlarged to three times its present volume.

[13] W. E. Deming, *Phil. Mag.*, **11**, 146 (1931).

[14] For the method of computation, suggested originally by Gauss see H. Schultz, *J. Am. Stat. Assoc.*, **25**, 139 (1930).

TABLE I

PROPORTIONAL PROBABLE ERROR OF COEFFICIENT OF THERMAL EXPANSION[a] (IN %)

x	$n = 15$	$n = 21$	$n = 25$	$n = 31$	$n = 35$	$n = 41$	$n = 45$
0	±0.38	±0.23	±0.18	±0.13	±0.11	±0.08	±0.07
2	.31	.21	.16	.12	.10	.08	.07
5	.62	.20	.14	.10	.09	.07	.06
7	1.33	.37	.19	.10	.08	.06	.06
10	....	.82	.42	.19	.12	.07	.06
12		....	.64	.28	.15	.10	.07
15			....	.47	.26	.16	.12
17				....	.40	.22	.15
20					....	.32	.22
22						....	.28

[a] Assumptions: (1) Coefficient of thermal expansion = 0.001 cc./g.-deg. (2) $v_t = a + bt + ct^2 + dt^3$. (3) Probable error of single observation of sp. vol. = $\pm 2.5 \times 10^{-5}$ cc./g.

Table I shows also that for any given value of x an increase in the number of observations causes a decrease in the probable error of the slope at a diminishing rate. Hence a table such as this helps one decide the number of observations demanded by a certain desired accuracy.

Experimental Data

Measurements of the coefficient of thermal expansion of benzene and of toluene (Sample C) were made with the weight dilatometer using the same samples that were used for the measurement[2] of $(\partial T/\partial P)_S$. The dilatometer was heated in the same oil thermostat used for the piezo-thermometric bomb, and so the temperature uncertainties were the same as previously listed,[2] namely: a probable error of ±0.02 up to 50°; ±0.03 from 50 to 80°; and ±0.02 from 80 to 110°. The weight[15] of liquid contained was computed from a weighing at 25° and the density of the liquid, for which the mean of a series of measurements with a 2-ml. Sprengel–Perkin pycnometer[16] at 1° intervals from 20 to 30° was used. Evidence that the liquids were air-free was furnished by the fact that successful measurements were made less than 1° below the normal b. p.

TABLE II

MEASUREMENTS WITH WEIGHT DILATOMETER CONTAINING BENZENE

$W_{25} = 20.9496$; $d'_{25} = 13.5335$; $d_{25} = 0.87387$. Therefore: $w = 3.5006$ g.; $w'_{25} = 17.4490$ g.

t, °C.	w^*, g.	v, cc./g.	$10^5 \times \Delta^a$
8.00	.....	1.12132	− 9
11.00	0.1918	1.12520	+ 2
14.00	.1988	1.12923	+ 2
17.05	.2007	1.13329	+10
20.00	.2023	1.13740	+ 2
23.00	.2040	1.14155	+ 1
25.00	.....	**1.14434**	....
26.00	.2057	1.14574	± 0
29.00	.2075	1.14997	− 1
32.00	.2085	1.15422	+ 1
35.00	.2107	1.15854	− 2
38.00	.2135	1.16291	− 5
41.00	.2125	1.16727	− 2
44.00	.2143	1.17166	+ 2
47.00	.2187	1.17616	± 0
50.00	.2220	1.18073	− 4
53.00	.2185	1.18524	+ 2
56.00	.2222	1.18982	+ 6
59.00	.2298	1.19458	− 3
68.02	.6904	1.20889	+ 1
71.00	.2308	1.21369	+ 6
74.00	.2400	1.21868	± 0
77.00	.2386	1.22366	± 0
80.00	.2439	1.22875	− 4

[a] Δ = *calcd.* minus *exptl.*

TABLE III

MEASUREMENTS WITH WEIGHT DILATOMETER CONTAINING TOLUENE

$W_{25} = 20.8059$ g.; $d'_{25} = 13.5335$; $d_{25} = 0.86220$. Therefore: $w = 3.4605$ g.; $w'_{25} = 17{,}3454$ g.

t, °C.	w^*, g.	v, cc./g.	$10^5 \times \Delta^a$
8.00	.....	1.13903	−4
11.00	0.1765	1.14262	−1
14.00	.1768	1.14623	+2
17.00	.1806	1.14992	±0
20.00	.1804	1.15361	+1
23.00	.1809	1.15731	+3
25.00	.....	**1.15983**	...
26.00	.1837	1.16108	+2
29.00	.1853	1.16489	−1
32.00	.1834	1.16866	+3
35.00	.1886	1.17247	+6
38.00	.1882	1.17643	−2
41.00	.1886	1.18033	−1
44.00	.1902	1.18426	+1
46.98	.1925	1.18825	−3
50.00	.1957	1.19231	−4
53.00	.1932	1.19632	±0
56.00	.1984	1.20045	−2
58.97	.1997	1.20461	−7
62.00	.2008	1.20880	−4
65.00	.2009	1.21299	±0
71.00	.4099	1.22157	+1
74.00	.2087	1.22594	+1
77.00	.2098	1.23035	+2
82.95	.4248	1.23929	±0
85.94	.2155	1.24383	+1
88.98	.2216	1.24851	±0
94.96	.4413	1.25785	+5
98.00	.2308	1.26274	±0
101.01	.2269	1.26755	+5
104.00	.2330	1.27251	−1
106.98	.2321	1.27745	−1
110.00	.2386	1.28254	−4

[a] Δ = *calcd.* minus *exptl.*

---

(15) All weights were corrected for air buoyancy.

(16) H. Sprengel, *J. Chem. Soc.*, **26**, 577 (1873); W. H. Perkin, *ibid.*, **45**, 421 (1884).

TABLE IV

NOTES ON PREVIOUS MEASUREMENTS OF THE COEFFICIENT OF THERMAL EXPANSION OF BENZENE AND OF TOLUENE

Observer	Method	Temp. control	No. obs.	Interval	Probable error $10^5 \times \Delta v$	Probable error $\Delta(\partial V/\partial T)_P$
	A. Benzene					
Biron[a]	Kopp dilatometer, 70 ml.	±0.01	11	*ca.* 17°	± 2.5	±0.4%
Tyrer[b]	Single-capillary pycn., 70 ml.	± .01	8	Very irreg.	?	±1%
Pesce[c]	Duplicate silica–glass dilatometer with Hg seal, 24 ml.	± .01	16 10	2°, 30 to 45° 5°, 65 to 80°	± 2.2	±0.4%
Goss[d]	Ostwald–Sprengel pycnometer	± .05	5	10°	± 5	±3%
Massart[e]	Thermometer-type dilatometers	?	7	15 or 20°	± 3	±1%
Cohen and Buij[f]	Dilatometer, 35 ml.	± .015	33	4°	± 3	±0.1%
	B. Toluene					
Tyrer[b]	Single-capillary pycn., 70 ml.	±0.01	11	Very irreg.	?	±1%
Jones and Jelen[g]	Weight dilatometer, Hg seal, 61 ml.	± .005	20	10°	± 1	±0.1%
Massart[e]	Thermometer-type dilatometers	?	14	10 to 20°	±12	±1.5%

[a] E. B. Biron, *J. Russ. Phys.-Chem. Soc.*, **42**, 135 (1910); *Chem. Zentr.*, 81, I, 1912 (1910). [b] D. Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914). [c] B. Pesce, *Gazz. chim. ital.*, **65**, 440 (1935). [d] F. R. Goss, *J. Chem. Soc.*, 727 (1935). [e] L. Massart, *Bull. soc. chim. Belg.*, **45**, 76 (1936). [f] E. Cohen and J. S. Buij, *Z. physik. Chem.*, **B35**, 270 (1937). [g] G. Jones and F. C. Jelen, THIS JOURNAL, **57**, 2532 (1935).

The specific volume was computed by equation (1) from the observed values of w^*, which are listed in Tables II and III. A cubic equation was fitted by the method of least squares to the values of the specific volume of each liquid. The results

$$[C_6H_6]\quad v_t = v_0 + 1.29651 \times 10^{-3}t + 1.7516 \times 10^{-6}t^2 + 5.930 \times 10^{-9}t^3 \quad (7)$$

$$[C_7H_8]\quad v_t = v_0 + 1.18497 \times 10^{-3}t + 1.0672 \times 10^{-6}t^2 + 7.366 \times 10^{-9}t^3 \quad (8)$$

are for benzene and toluene, respectively. The residuals with respect to these equations are listed in the last columns of Tables II and III. The probable error of an individual observation, based on the residuals, is $\pm 3.0 \times 10^{-5}$ cc./g. for benzene and $\pm 2.0 \times 10^{-5}$ cc./g. for toluene. Each of these values is somewhat less than the *a priori* estimate given on page 692.

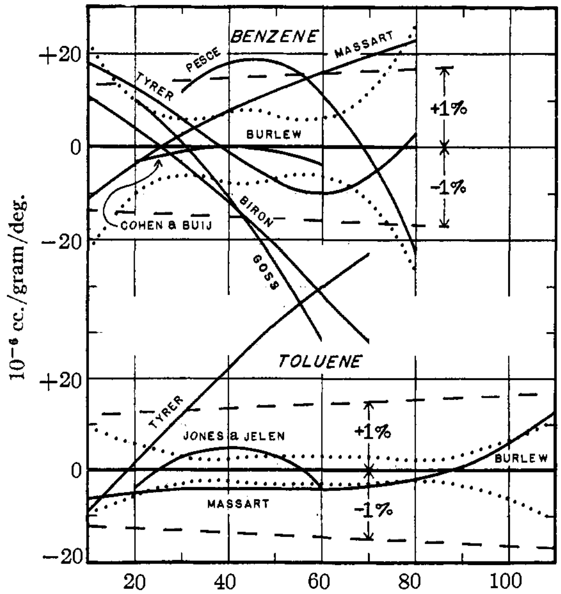

Fig. 2.—Deviations of expansion coefficients.

Differentiation of equations (7) and (8) yielded the following pair of equations for the coefficients of thermal expansion of benzene and of toluene, respectively

$$[C_6H_6]\quad 1000\ (\partial V/\partial T)_P = 1.2965 + 3.503 \times 10^{-3}t + 1.779 \times 10^{-5}t^2 \quad (9)$$

$$[C_7H_8]\quad 1000\ (\partial V/\partial T)_P = 1.1850 + 2.134 \times 10^{-3}t + 2.210 \times 10^{-5}t^2 \quad (10)$$

The values of the coefficients of thermal expansion, computed from these two equations at 5° intervals, are listed in Table II of the paper[17] on the heat capacity of these liquids.

Comparison of Data for $(\partial V/\partial T)_P$.—The deviations (*other observer* minus *Burlew*) of the results of other investigators from these values are shown in Fig. 2.[18] A summary of the accuracy[19] of their work is given in Table IV, in terms of an estimate of the probable error of $(\partial V/\partial T)_P$ that I have deduced from each author's stated or implied estimate of the probable error of his values of the specific volume. In only three of those investigations (Pesce, Cohen and Buij, and Jones and Jelen) was a sufficient number of observations of specific volume made at regular intervals to permit the

---

(17) J. S. Burlew, THIS JOURNAL, **62**, 696 (1940).

(18) In each graph of Fig. 2 three times the probable error of the present data is represented by a pair of dotted lines that are symmetrical with respect to the base lines.

(19) A measurement of the coefficient of thermal expansion of a liquid practically is unaffected by systematic errors in the specific volume. Hence its accuracy depends solely on the precision of the measurements of the specific volume.

computation of accurate values of the coefficient of thermal expansion. The deviations of the present data from each of those three are well within the limits of the sum of three times the probable error of each set of data. The results of Massart also agree well with mine, and those of the other four do not disagree by more than the experimental uncertainty except at the ends of the range.

In addition to the data on $(\partial V/\partial T)_P$ that are referred to in Fig. 2, there exist the results of density measurements over considerable ranges of temperature that have not been represented by equations. Although the corresponding coefficients of thermal expansion could not be evaluated accurately, a comparison of total expansions has been made, as shown in Table V. There is good agreement with all except the results of Perkin, whose extremely small expansions are inexplicable. Also the present value for the specific volume of benzene at the boiling point is in close agreement with that of Arbusov.[20] The values of Neubeck[3b] for both benzene and toluene were slightly larger than the present ones.

TABLE V

TOTAL EXPANSION OF BENZENE AND OF TOLUENE

Observer	Range	Expansion, cc./g.	$10^4 \times \Delta$
	A. Benzene		
Perkin[a]	10 to 70°	0.0612	−270
Young[b]	10 to 70°	.0882	± 0
	70 to 80°	.0154	− 12
Meyer and Mylius[c]	15.8 to 72.7°	.0847	− 1
Timmermans and Martin[d]	15 to 30°	.02052	+ 2.5
	30 to 60°	.04461	+ 1.4
	B. Toluene		
Perkin[a]	10 to 100°	0.0727	−519
Timmermans and Martin[d]	15 to 30°	.01859	− 0.8
	30 to 60°	.03964	− 1.8

[a] W. H. Perkin, *J. Chem. Soc.*, **69**, 1025 (1896). [b] S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1909). [c] J. Meyer and B. Mylius, *Z. physik. Chem.*, **95**, 349 (1920). [d] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926).

Density of Toluene at 0 and 25°

An examination of the literature has revealed considerable variance among the values for the density of toluene, which does not seem to have been commented on previously. The several measurements of the density of toluene at 0 and 25° and the measured expansions between these two temperatures are summarized in Table V. The present value of the expansion agrees well with two of the others, inasmuch as the limit of accuracy is ±0.00001, imposed by the uncertainty of ±0.01° in the temperature scale. The several values of the density, however, are at considerable variance, so that a redetermination of the absolute density at both 0 and 25° of several samples of toluene differently prepared clearly is needed.

TABLE VI

DENSITY OF TOLUENE AT 0 AND 25°

Observer	d_0, g./ml.	d_{25}, g./ml.	$v_{25} - v_0$, ml./g.
Timmermans[a]	0.88448		
Tyrer[b]	.88412		0.03030
Timmermans and Martin[c]	.88545	0.86234	.03027
Kelley[d]	.88456		
Massart[e]	(.88545)		.03020
Smith and Wojciechowski[f]		.86174	
Burlew (this research)	.8854	.8622	.03031

[a] J. Timmermans, *Sci. Proc. Roy. Dublin Soc.*, **13**, 310, (1911–13), p. 354; *Bull. soc. chim. Belg.*, **26**, 205 (1912). This is the value listed in "Int. Crit. Tables," Vol. III, pp. 29 and 33. [b] D. Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914), p. 2540. The expansion has been computed from his empirical equation. [c] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926), p. 752. The density at 25° had been interpolated linearly by the authors from measurements at 15 and 30°. [d] K. K. Kelley, THIS JOURNAL, **51**, 2738 (1929). [e] L. Massart, *Bull. soc. chim. Belg.*, **45**, 76 (1936), p. 83. The density at 0° was an arbitrary base point and not a new determination. The expansion has been computed from his empirical equation. [f] E. R. Smith and M. Wojciechowski, *Bull. intern. acad. polon. sci.*, **1936A**, 123.

Summary

A weight dilatometer for the measurement of the coefficient of thermal expansion of 5 cc. of a volatile liquid over a wide range of temperature with a probable error of a few tenths of one per cent. has been described, and its manipulation has been outlined. An analysis has been given of the factors, including the number of observations, that affect the precision of the measurement of the coefficient of thermal expansion. Data for $(\partial V/\partial T)_P$ of benzene and of toluene from 8° to the respective boiling points have been presented and compared with the results of previous investigators. Discrepancies in the current values for the density of toluene at 0 and 25° have been pointed out.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 21, 1939

---

(20) A. E. Arbusov, *Z. physik. Chem.*, **131**, 49 (1927), p. 59.