[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Measurement of the Heat Capacity of a Small Volume of Liquid by the Piezo-Thermometric Method. III. Heat Capacity of Benzene and of Toluene from 8°C. to the Boiling Point

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As a first application of the piezo-thermometric method of measuring the heat capacity of a small volume of liquid, the heat capacity of benzene and of toluene was determined. Not only did these results furnish an opportunity for comparison with those obtained by other methods by other investigators, but also they extended the data concerning these two liquids.

Method.—The piezo-thermometric method[2] is based on the following thermodynamic equation

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

The heat capacity of each liquid was computed according to equation (1) at each temperature[3] at which a measurement of the adiabatic temperature-pressure coefficient, $(\partial T/\partial P)_S$, had been made, with the results given in Table I. The corrected experimental values of $(\partial T/\partial P)_S$ which are listed in the next to the last column of Tables III and IV of Ref. (2) were employed, in order that no spurious trend might be given to the values of c_p by the use of calculated values of $(\partial T/\partial P)_S$. The coefficients of thermal expansion, $(\partial V/\partial T)_P$, were computed from the equations[4a] that had been obtained by differentiation of the empirical equations used to express the results of measurements of the specific volumes of these two liquids made at 3° intervals from 8° to the respective boiling points. For the computation of the absolute temperature T in equation (1) the ice point was taken as 273.2° K.

TABLE I

HEAT CAPACITY OF BENZENE AND OF TOLUENE

Temperature		Benzene			Toluene		
°C.	°K.	c_p, j./g.-deg.	p	$10^4 \times \Delta^a$	c_p, j./g.-deg.	p	$10^4 \times \Delta^a$
7.8	281	1.6861	1	−10	1.6606	1	+41
10.8	284	1.6931	2	− 4	1.6686	2	+16
13.8	287	1.6991	3	+17	1.6746	2	+21
16.8	290	1.7101	4	− 8	1.6837	2	− 4
19.8	293	1.7207	6	−26	1.6936	3	−29
22.8	296	1.7276	8	− 3	1.7002	4	−16
25.8	299	1.7367	10	0	1.7088	5	−17
28.8	302	1.7478	11	−15	1.7150	6	+10
31.8	305	1.7559	11	+ 3	1.7272	7	−19
34.8	308	1.7657	10	+ 6	1.7368	7	−17
37.8	311	1.7770	8	− 6	1.7442	8	+10
40.8	314	1.7834	7	+33	1.7537	8	+19
43.8	317	1.7964	7	+ 7	1.7645	8	+18
46.8	320	1.8068	7	+ 6	1.7735	8	+38
49.8	323	1.8182	8	− 4	1.7909	7	−25
52.8	326	1.8312	10	−31	1.8013	7	−15
55.8	329	1.8413	11	−29	1.8095	7	+18
58.8	332	1.8467	11	+18	1.8229	7	0
61.8	335	1.8561	10	+24	1.8346	7	0
64.8	338	1.8612	8	+71	1.8450	7	+13
67.8	341	1.8828	6	−49	1.8610	7	−30
70.8	344	1.8896	4	−23	1.8706	8	− 9
73.8	347	1.8971	3	− 8	1.8805	8	+ 8
76.8	350	1.9050	2	0	1.8955	8	−27
79.8	353	1.9075	1	+59	1.9047	8	− 5
82.8	356				1.9159	7	− 5
85.8	359				1.9254	7	+10
88.8	362				1.9336	6	+35
91.8	365				1.9475	5	0
94.8	368				1.9562	4	+15
97.8	371				1.9668	3	+ 6
100.8	374				1.9775	2	− 7
103.8	377				1.9861	2	− 3
106.8	380				1.9963	2	−21
109.8	383				2.0035	1	−13

[a] Δ = *calcd.* minus *exptl.*

Precision.—The uncertainty of a value of c_p determined according to equation (1) is a combination of the uncertainties that are contributed by each of the factors on the right-hand side of that equation. Those for $(\partial T/\partial P)_S$ have been summarized in Table II of Ref. 2. As explained elsewhere[5] the observational uncertainty in $(\partial V/\partial T)_P$ depends on the number of observations of specific volume and also varies over the temperature range. Combination of these several uncertainties gave for the estimated observational probable error of c_p of benzene and of toluene ± 0.25%

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[2] For a discussion of this method see the first paper of this series, THIS JOURNAL, **62**, 681 (1940).

[3] These measurements had been made at 3° intervals; but the precision was so great over the whole range of temperature that now it is considered that measurements at ten to fifteen uniformly distributed temperatures would have been sufficient to yield results for $(\partial T/\partial P)_S$ comparable in precision to those obtained for $(\partial V/\partial T)_P$ by twice that number of measurements of the specific volume.

[4] J. S. Burlew, THIS JOURNAL, **62**, 690 (1940); (a) equations (9) and (10).

[5] Ref. (4), p. 692. Table I of Ref. (4) shows the extent of the variation of the probable error with temperature for a particular number of observations. The estimates of the probable error of $(\partial V/\partial T)_P$ for benzene and toluene are only 60 to 80% as large as the table indicates for $n = 23$ and 32, respectively, because $(\partial V/\partial T)_P$ of both liquids is greater than 0.001 cc./g.-deg.

at the middle of the range, somewhat less on either side of the middle, and about twice as much at the ends[6] of the range. The estimated systematic probable error of c_p was ±0.20% over the entire range.

c_p as a Function of Temperature.—The curves obtained by plotting as functions of the temperature the values of c_p listed in Table I are slightly S-shaped, the change of curvature being more pronounced for toluene than for benzene. It was proved by means of a calculation of the specific volume from computed values of the heat capacity that this change of curvature was greater than could be accounted for on the assumption that errors in the measurements of specific volume gave rise to false values of $(\partial V/\partial T)_P$.

Before equations were derived for these curves, it was necessary[7] to weight the individual values of c_p, because the probable error was not constant. The weights listed under p in Table I were taken in proportion to the reciprocal of the square of the estimated probable error of each point. The cubic equations based on the weighted points are

$$[\mathrm{C_6H_6}]\ c_p = 1.6673 + 2.047 \times 10^{-3}t + 3.051 \times 10^{-5}t^2 - 2.196 \times 10^{-7}t^3 \quad (2)$$

$$[\mathrm{C_7H_8}]\ c_p = 1.6534 + 1.119 \times 10^{-3}t + 4.294 \times 10^{-5}t^2 - 2.204 \times 10^{-7}t^3 \quad (3)$$

The residuals with respect to these equations are listed in Table I. The probable error of an individual observation in the middle of the range, computed from these residuals, is ±0.08% in the case of benzene and ±0.05% in the case of toluene. Both of these values are considerably smaller than the *a priori* estimate given above, which is to be expected, because the values of $(\partial V/\partial T)_P$ used in computing c_p had been smoothed by the process of differentiation. When the unit of c_p is changed from the joule to the defined 15°-calorie,[8] equations (2) and (3) become

$$[\mathrm{C_6H_6}]\ c_p = 0.3984 + 4.89 \times 10^{-4}t + 7.29 \times 10^{-6}t^2 - 5.25 \times 10^{-8}t^3 \quad (4)$$

$$[\mathrm{C_7H_8}]\ c_p = 0.3951 + 2.68 \times 10^{-4}t + 1.026 \times 10^{-5}t^2 - 5.27 \times 10^{-8}t^3 \quad (5)$$

Comparison of Data.—Values of c_p at 5°, intervals, computed from equations (4) and (5), are listed in Table II. They are compared with previous data[9] in Fig. 1, which shows the deviations (*other observer* minus *Burlew*) in millical. of those data that extend over any considerable temperature range. Table III summarizes the most pertinent information concerning the types of measurements that had been carried out in arriving at those values. In nearly all cases the estimated probable error listed in the last column is based on the original author's estimate of the accuracy of his measurements. In Fig. 1 the circles distributed along the two zero base lines indicate the individual values of c_p that are listed

TABLE II

COEFFICIENT OF THERMAL EXPANSION, TEMPERATURE-PRESSURE COEFFICIENT, AND HEAT CAPACITY OF BENZENE AND OF TOLUENE

t, °C.	$1000(\partial V/\partial T)_P$ cc./g.-deg.		$100(\partial T/\partial P)_S$ deg./bar		c_p cal./g.-deg.	
	C_6H_6	C_7H_8	C_6H_6	C_7H_8	C_6H_6	C_7H_8
5	1.314	1.196	2.180	2.012	0.4010	0.3967
10	1.333	1.209	2.234	2.056	.4040	.3987
15	1.353	1.222	2.288	2.100	.4072	.4012
20	1.374	1.237	2.343	2.144	.4107	.4041
25	1.395	1.252	2.398	2.189	.4144	.4074
30	1.418	1.269	2.455	2.235	.4182	.4109
35	1.441	1.287	2.513	2.282	.4222	.4148
40	1.465	1.306	2.572	2.331	.4263	.4188
45	1.490	1.326	2.633	2.380	.4304	.4231
50	1.516	1.347	2.696	2.431	.4345	.4275
55	1.543	1.369	2.760	2.484	.4386	.4321
60	1.571	1.393	2.828	2.538	.4427	.4367
65	1.599	1.417	2.897	2.595	.4466	.4414
70	1.629	1.443	2.970	2.654	.4504	.4460
75	1.659	1.469	3.045	2.715	.4540	.4506
80	1.691	1.497	3.123	2.778	.4573	.4552
85		1.526		2.845		.4596
90		1.556		2.914		.4639
95		1.587		2.986		.4679
100		1.619		3.061		.4718
105		1.653		3.140		.4753
110		1.687		3.222		.4786

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[6] Unless it is feasible to make measurements of specific volume over a wider range of temperature than it is desired to evaluate the coefficient of thermal expansion, one must be resigned to have the probable error of c_p determined by the piezo-thermometric method two to three times as great at the ends of the range as in the middle.

[7] W. E. Deming, *Phil. Mag.*, **11**, 146 (1931). When cubic equations for c_p are derived using equal weights, the individual parameters are somewhat different, but the interpolated values of c_p are not much different from those computed according to equations (2) and (3), respectively. The greatest differences occur at the ends. In the case of benzene, the value at 10° is lowered 0.2 millical. and that at 80° is raised 0.6 millical. by the weighting; whereas in the case of toluene the effect is opposite, the value at 10° being raised 0.3 millical. and that at 110° being lowered 0.3 millical.

[8] Calorie_{15} = 4.1850 absolute joules. F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 9.

[9] Whenever necessary and possible the data have been corrected to the defined 15°-calorie. In addition it has been necessary to recompute the data of von Reis and of Mills and MacRae, because the equations they published had been derived without regard to all their data. The new equations, evaluated by the method of least squares from all the original data, are

$$[\mathrm{C_6H_6}\text{—von Reis}]\ c_p = 0.3853 + 9.0 \times 10^{-4}t \quad (6)$$

$$[\mathrm{C_7H_8}\text{—von Reis}]\ c_p = 0.3985 + 6.7 \times 10^{-4}t \quad (7)$$

$$[\mathrm{C_6H_6}\text{—Mills and MacRae}]\ c_p = 0.39593 + 5.72 \times 10^{-4}t \quad (8)$$

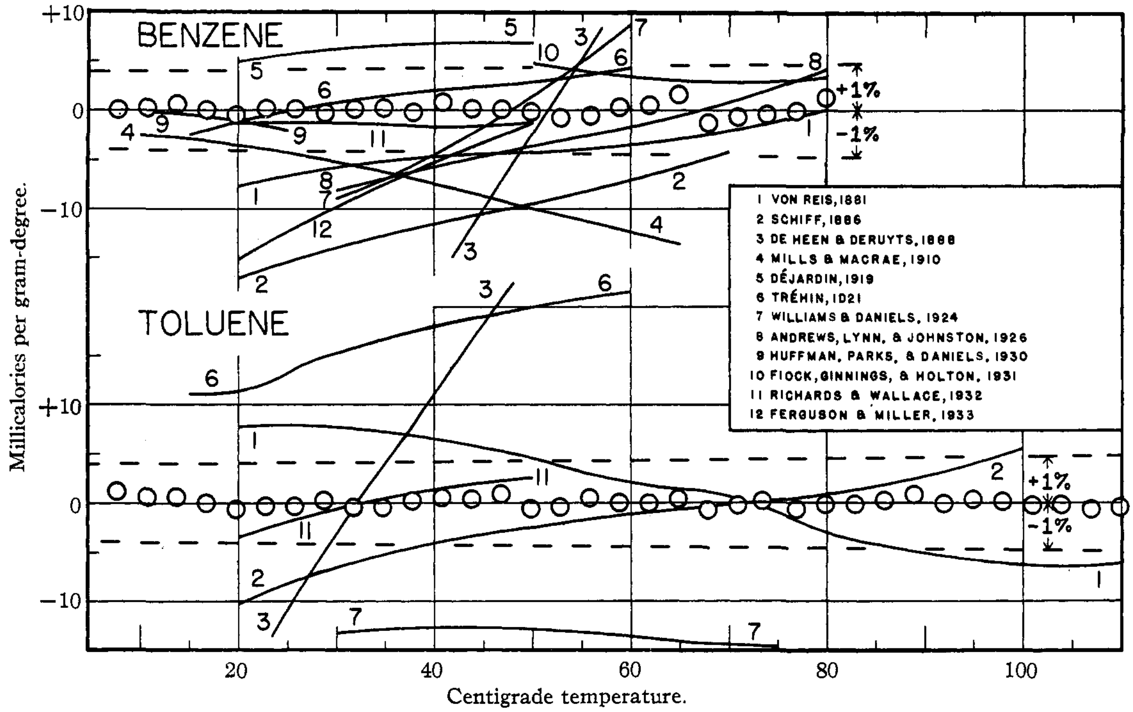

Fig. 1.—Deviations of heat capacities.

TABLE III

NOTES TO ACCOMPANY FIGURE 1

Curve[a]	Method	Sample, g.	Interval,[b] deg.	Detn.	Prob. error, %
1	Method of mixtures: 90 g. H_2O in calorimeter at 20°	5	23 to 96	7	±1.0
2	Method of mixtures: 500 g. H_2O in calor. at 6 to 15°	58	48 to 88	10	±1.0
3	Cooling method	?	5	12	±2
4	Unstirred, elec. heated, adiabatic calorimeter (500 ml. Dewar flask)	393	10	15	±0.2
5	Unstirred, elec. heated, adiabatic calorimeter (2 Dewar flasks)	100	5 to 10	16	± .4
6	Unstirred, elec. heated, adiabatic calorimeter	100	*ca.* 4	?	± .3
7	Stirred, elec. heated adiabatic calorimeter with controlled thermal head	140	6	12	± .1
8	Method of mixtures: kerosene calor. at 22° calibrated with a bar of silver	3	8 to 88	11	± .5
9	Nernst aneroid adiabatic calorimeter	35	1 to 5	6	± .4
10	Stirred, elec. heated, adiabatic, pressure calor. with controlled thermal head	?	10	36	± .5
11	Piezo-thermometric method	?	0.4 to 0.7	8	± .2
12	Method of balanced cooling	900	5 to 10	11	± .3

[a] The sources of data are (1) M. A. von Reis, *Ann. Physik*, **13**, 447 (1881); (2) R. Schiff, *Ann.*, **234**, 300 (1886); (3) P. deHeen and F. Deruyts, *Bull. classe sci. Acad. roy. Belg.*, **15**, 168 (1888); (4) J. E. Mills and D. MacRae, *J. Phys. Chem.*, **14**, 797 (1910); (5) G. Déjardin, *Ann. phys.*, [9] **11**, 253 (1919); (6) R. Tréhin, *ibid.*, **15**, 246 (1921); (7) J. W. Williams and F. Daniels, THIS JOURNAL, **46**, 903 (1924); (8) D. H. Andrews, G. Lynn and J. Johnston, *ibid.*, **48**, 1274 (1926); (9) H. M. Huffman, G. S. Parks and A. C. Daniels, *ibid.*, **52**, 1547 (1930); (10) E. F. Fiock, D. C. Ginnings and W. B. Holton, *Bur. Standards J. Research*, **6**, 881 (1931); (11) W. T. Richards and J. H. Wallace, THIS JOURNAL, **54**, 2705 (1932); (12) A. Ferguson and J. T. Miller, *Proc. Phys. Soc.* (London), **45**, 194 (1933).

[b] The temperature interval through which the liquid was heated or cooled during a single experiment.

in Table I. The radius of each circle is 1 millical., which is approximately the estimated probable error of a single observation in the middle two-thirds of the range.

The present data differ by less than 1% from the mean of all the previous measurements[10] shown in Fig. 1 (neglecting the results of deHeen and Deruyts); but there are great differences among the results of the various investigators, for which no reason is apparent. Although some samples may have been more pure than others, there probably was no gross impurity present in any, for all had been especially purified. What impurities did remain probably would have changed c_p by not more than 0.5%.

The comparison with the work of the early investigators von Reis, Schiff, and deHeen and Deruyts is important, because it furnishes an estimate of the worth of their values of the heat capacity of the many liquids that they alone investigated. The results of deHeen and Deruyts appear worth-

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(10) The close agreement between the present results and those of Richards and Wallace is partly accidental, because some of the difference between their values of $(\partial T/\partial P)_S$ and the present ones happened to be balanced by an opposite difference between the present measurements of $(\partial V/\partial T)_P$ and the values that they had taken from the "Int. Crit. Tables."

less. Those of von Reis and of Schiff[11] are within ±2% or ±3% of the truth, if their results for benzene and toluene are fair samples of their work.

In addition to the measurements over a considerable range of temperature recorded in Fig. 1, there have been a considerable number of others. Some[12] of the early ones consisted of only a few measurements by the method of mixtures. Others[13] were just incidental to the investigation of c_p of solutions. Still other measurements[14] made at isolated temperatures involved either single experiments of unverified precision or samples of unknown purity. All these miscellaneous data have been compared with the present results; but the details are scarcely worth recording. Just as those different results show considerable variance among themselves, so the present ones agree with some of them and disagree with others.

Although equation (3) is not suitable for extrapolation to low temperatures, the present data for toluene are consistent with those of Battelli[15] and of Kelley[16] at low temperatures, as can be seen when the several sets of data are plotted on the same graph. Kelley's value at 11.3°, which was the upper limit of temperature in his measurements, is only 2 millical. (0.5%) lower than the present one.

Minimum in c_p of Benzene.—Williams and Daniels,[17] shortly after the publication of the data referred to in Fig. 1, published the results of further experiments with the same calorimeter. They found that the c_p *vs.* t curve of dry samples of benzene exhibited at about 20° a minimum with slight curvature, which they considered indicative of molecular changes in the liquid. A sample saturated with moisture at 6° (0.035% H_2O), however, showed only a marked decrease in slope in the vicinity of 20°. Unfortunately they were not able to trace the course of the curve very far on the low-temperature side of the minimum. The present results, which extend 12° below 20°, give no indication of a minimum. The curve is slightly S-shaped, as mentioned above, which means that the slope is a little less at the low-temperature end than in the middle; but the decrease is not nearly so marked as was found by Williams and Daniels for even a moist sample.

Le Blanc and Möbius,[18] using a heating interval of only 0.1° with a Nernst vacuum calorimeter, made measurements of c_p both above and below the m. p. of a highly purified sample of 75 g. of benzene. Their values at 30.15 and 25.15° (each the mean of two determinations) were 2 and 3 millical., respectively, less than those computed from equation (4). At 14.90° the mean of their twelve determinations was only 1 millical. (0.25%) greater than that computed from equation (4). This value they considered a minimum on the c_p *vs.* t curve, because the mean of five determinations at 6.95° was 6 millical. higher than it and the mean of eighteen determinations at 5.75° was 5 millical. higher. The presence of the minimum they ascribed to the persistence of a state of partial order above the m. p. According to the present data c_p continues to decrease regularly with decreasing temperature down to the limit of the measurements at 7.8°. The present value at this temperature is 11 millical. less than the value found by Le Blanc and Möbius at 6.95°.

Cohen and Buij[19] made triplicate measurements of c_p of carefully purified benzene at 4° intervals from 8 to 24°, in a search for irregularities in the c_p *vs.* t curve. Their conclusion that the curve is linear in this temperature interval is supported by the present data. Their values of c_p were not absolute ones, but were relative to the value 0.4078 cal./g. at 20°, given by Williams and Daniels,[17] which is 0.0028 cal. lower than that found in the present investigation. If the straight line used by Cohen and Buij to express their data is shifted so that it passes through the present value at 20°, their results at other temperatures between 8 and 24° differ from those computed

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(11) Schiff's conclusion (*Ann.*, **234**, 300 (1886), p. 327), sometimes referred to as "Schiff's Law," that the specific heat of the different members of a homologous series can be represented by a single straight line or by a few parallel straight lines, is not valid for the two homologs benzene and toluene, as can be seen from Table I. In the "Int. Crit. Tables," nevertheless, twenty-five paraffin esters of the fatty acids are listed on the authority of Schiff as having a heat capacity at 20° of 1.921 j./g., with an uncertainty of only ±0.5%.

(12) (a) *Benzene:* H. V. Regnault, *Mém. acad. sci. inst. imp.* (France), **23**, 3 (1862), p. 283; S. U. Pickering, *Proc. Roy. Soc.* (London), **49**, 11 (1890). (b) *Toluene:* F. L. Perrot, *Arch. sci. phys. nat.*, **32**, 145, 254, 337 (1894); W. Siivola, *Översikt av Finiska vetenskaps-societeten förhandlingar*, **56A**, no. 8 (1913), 13 pp.

(13) J. H. Schüller, *Ann. Physik, Erg. Bd.*, **5**, 116, 192 (1871); C. Forch, *Ann. Physik*, [4] **12**, 202 (1903); A. Schulze, *Ber. deut. physik. Ges.*, **14**, 189 (1912).

(14) (a) *Benzene:* A. Schlamp, *Ann. Physik*, (n. f.) **58**, 759 (1896); W. G. Marley, *Proc. Phys. Soc.* (London), **45**, 591 (1933). (b) *Toluene:* T. Estreicher and M. Staniewski, *Bull. intern. acad. sci. Cracovie. Classe Sci., math., nat. A.*, 834 (1912). (c) *Benzene and toluene:* Timofeev, *Chem. Zentr.*, **76**, II, 429 (1905); R. W. B. Stephens, *Phil. Mag.*, **17**, 297 (1934).

(15) A. Battelli, *Physik. Z.*, **9**, 671 (1908).

(16) K. K. Kelley, THIS JOURNAL, **51**, 2738 (1929).

(17) J. W. Williams and F. Daniels, THIS JOURNAL, **46**, 1569 (1924).

(18) M. Le Blanc and E. Möbius, *Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math.-phys. Klasse*, **85**, 75 (1933).

(19) E. Cohen and J. S. Buij, *Z. physik. Chem.*, **B35**, 270 (1937).

from equation (4) by not more than 0.2 millical. (0.05%), which is excellent agreement with respect to the temperature coefficient of c_p.

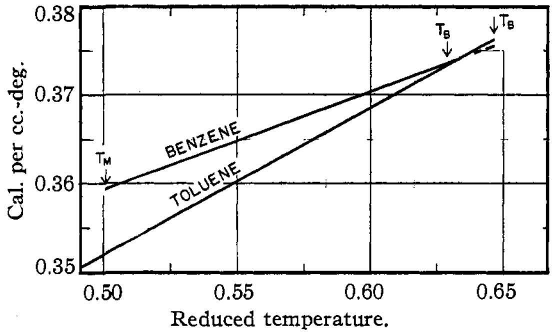

Fig. 2.—Heat capacity per unit volume.

Heat Capacity per Unit Volume

Williams and Daniels[20] suggested on the basis of their data that "the heat capacity per cubic centimeter of unassociated liquids is a constant, approximately 0.35 calorie per degree at room temperature and slightly more than this at higher temperatures." The present data are especially suitable for a test of this suggestion. The values[21] of c_p in cal. per cc., computed at each temperature at which a measurement of $(\partial T/\partial P)_S$ had been made, varied much less with the temperature than the corresponding values of c_p in cal. per gram; but they were by no means constant for either liquid over the whole temperature range nor were they the same for both liquids at the same temperatures. The variation with temperature was expressed by these two linear equations

$$[C_6H_6]\ c_p\ (\text{cal./cc.-deg.}) = 0.3579 + 1.97 \times 10^{-4}t \quad (9)$$

$$[C_7H_8]\ c_p\ (\text{cal./cc.-deg.}) = 0.3453 + 2.79 \times 10^{-4}t \quad (10)$$

The fit of these equations was better than that of linear equations for c_p in cal. per gram. Thus the probable error of an individual observation based on the residuals was 4% less for equation (9) than for the corresponding one for c_p in cal. per gram and 28% less for equation (10). The straight lines represented by equations (9) and (10) approach each other at higher temperatures, but they do not intersect within the normal liquid range.

When the temperature variable in equations (9) and (10) is changed to the reduced temperature (that is, the absolute temperature divided by the absolute temperature of the critical point), the relative slopes of the lines are scarcely changed, but the line for toluene is shifted to the left, so that the two lines intersect as shown in Fig. 2. The reduced temperature of the point of intersection (0.635) is in good agreement with the conclusion of Schiff[22] that at six-tenths of the critical temperature equal volumes of homologous liquids (in his case 27 esters of fatty acids) have equal heat capacities.

Alleged Allotropy of Benzene

It is desirable to emphasize that the data presented in this series of three papers contradict the several suggestions that have been made concerning irregularities in the variation of the physical properties of benzene with temperature. Not only was no minimum observed in the c_p *vs.* t curve, as discussed above, but also comparison of the observations of $(\partial T/\partial P)_S$ and of the specific volume of benzene with those of toluene show the former to vary just as regularly in the neighborhood of 40° as the latter. This conclusion, which is in opposition to the suggestion that Menzies and Lacoss[23] made after an examination of the data of others for several physical properties, agrees with the measurements by Pesce[24] of the specific volume and the refractive index and with those of the specific volume by Cohen and Buij,[19] all of which had been made for the purpose of testing the suggestion of Menzies and Lacoss.

Acknowledgment.—It is a pleasure to thank my wife, Grace Schaum Burlew, for assistance in the computation of these data and in the preparation of the manuscript.

Summary

Values of the heat capacity of benzene and of toluene, computed from $(\partial V/\partial T)_P$ and $(\partial T/\partial P)_S$ measured with 5-cc. samples at 3° intervals from 8° to the respective boiling points, have been shown to agree with results by other investigators. No evidence has been found to support the suggestion that benzene is allotropic.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 21, 1939

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[20] J. W. Williams and F. Daniels, THIS JOURNAL, **46**, 903 (1924).

[21] Each such value is the same as that which would have been obtained if $(1/V_t)(\partial V/\partial T)_P$ had been substituted for $(\partial V/\partial T)_P$ in equation (1).

[22] R. Schiff, *Ann.*, **234**, 300 (1886), p. 330.

[23] A. W. C. Menzies and D. A. Lacoss, *Proc. Nat. Acad. Sci. U. S.*, **18**, 145 (1932).

[24] B. Pesce, *Gazz. chim. ital.*, **65**, 440 (1935).