THE SPECIFIC HEAT OF LIQUID BENZOL AND OF ITS SATURATED VAPOR

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Many measurements of the specific heat of different liquids have been made by various observers. If these measurements are examined it will be found that they contribute but little to any real knowledge of the laws that govern the energy changes involved. Isolated measurements have in many cases been made upon substances whose remaining physical constants are almost totally unknown. Such measurements, even if accurate, aid little in understanding the changes involved. Confining the attention to the thirty-odd liquids whose physical constants, such as the vapor pressure, density of the liquid and density of the saturated vapor at definite temperatures, and the critical data, have been carefully measured, one finds that for most of these liquids no measurements of the specific heat have been made. Isolated measurements¹ of the specific heat have been made upon hexane, heptane, octane, chlor-benzol, and methyl and ethyl formates. Somewhat more extended measurements¹ have been made upon water, methyl, ethyl and propyl alcohols, acetic acid, ether, isopentane, carbon dioxide, carbon disulphide, chloroform and benzol. A careful examination of these measurements makes it clear that more accurate and more extended work upon the specific heat of liquids is necessary before the subject can be discussed authoritatively. It was finally decided to measure the specific heat of benzol accurately and to plan for a future extension of the measurements over a wider range of temperature and to other substances.

The measurements of the specific heat of solid and liquid benzol obtained by previous workers are plotted and shown

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¹ Landolt, Börnstein, and Meyerhoffer's *Physikalisch-chemische Tabellen*. A. Battelli: *Phys. Zeit.*, 9, 671 (1908). *Nuovo Cimento*, (5) 13, 418 (1907). *Rend. Accad. Lincei*, (5) 16, I, 243 (1907). G. Teichner: *Drude's Ann.*, 13, 611 (1904). C. Dieterici: *Ibid.*, 12, 154 (1903).

in Fig. 1. The diversity of results shown makes clear the necessity for the experimental work described below.

Several years ago one of the authors experimented with a Dewar beaker as a calorimeter and found that under the conditions of use it much surpassed in efficiency calorimeters

Fig. 1

- 1 Regnault: *Mém. de l'Acad.*, 26, 262 (1862).
- 2 Schüller: *Pogg. Ann., Ergänzt.*, 5, 125 (1871).
- 3 W. Fischer: *Wied. Ann.*, 28, 400 (1886).
- 4 R. Schiff: *Liebig's Ann.*, 234, 300 (1886).
- 5 P. DeHeen and F. Deruyts: *Bull. Acad. Belg.*, (3) 15, 168 (1888).
- 6 S. U. Pickering: *Proc. Roy. Soc.*, 49, 11 (1890).
- 7 Jos. Ferche: *Diss. Halle*, 1890, *Wied. Ann.*, 44, 365 (1891).
- 8 A. Schlamp: *Ber. Oberhess. Ges. Naturw. u. Heilk.*, 31, 100 (1895).
- 9 C. Forch: *Drude's Ann.*, 12, 202 (1903).
- 10 A. Bogojawlenski: *Chemisches Centralblatt*, 76, 11, 945 (1905). *Schriften d. Dorpater Naturfor. Ges.*, 13, 1 (1904).
- 11 P. Nordmeyer and A. L. Bernouilli: *Verh. deutsch. phys. Ges.*, 9, 175 (1907).
- 12 Mills and MacRae.

in use up to that time. Dewar vessels have been rather frequently used for calorimetric work at low temperatures and since the investigation above cited was begun their use at ordinary temperatures purely as a calorimeter has been several times noted.¹ It was therefore decided to make use of a Dewar flask as a calorimeter, to fill the same nearly to the neck with a weighed quantity of benzol, and heat the benzol by means of a current of electricity passed through a platinum wire coil immersed in the benzol. The rise in temperature of the benzol and the heat added are determined. The calorimeter constant is separately determined by substituting water in the place of the benzol. The specific heat of the benzol can then be calculated. After much preliminary experimenting the details of the method were satisfactorily adjusted. The details of the apparatus and the various corrections necessary are described below.

The Dewar Flask.—The cooling curves of a series of double- and of triple-walled vacuum silvered Dewar flasks of 250 (double-walled only), 500 and 1000 cc capacity when filled with water up to the neck, were investigated, both when the flasks were stoppered and when they were open. The best of these flasks proved to be a 500 cc double-walled flask. That this flask should have proven better than the triple-walled flasks of the same, and of the larger size, was a matter of surprise, and indicated that there is considerable difference in the efficiency of flasks obtained from the same factory. The rate of cooling was greatly decreased when the flasks were stoppered and for this reason it was deemed best to use a very tightly stoppered flask, all evaporation from the flask being prevented.

The Platinum Wire Coil.—A small platinum wire was carefully coiled and the ends sealed into two glass tubes which were filled with mercury and passed through a suitable rubber stopper. The resistance of this coil was care-

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¹ L. J. Henderson and C. T. Ryder: *Science*, **27**, 743 (1908). H. C. Dickinson, E. F. Mueller and E. B. George: *Bull. Bureau Standards*, **6**, 379. J. Duclaux: *Comptes rendus*, **146**, 120 (1908).

fully determined at a number of temperatures by means of the usual Wheatstone's bridge arrangement—the bridge having been previously calibrated. The resistance was found to vary linearly with the temperature between the values, 1.1975 ohms at 0° C and 1.5365 ohms at 100° C. Subsequently another coil of approximately the same resistance was used, but as it was found that the resistance of the wire when immersed in a liquid varied with the current passed through the wire, and also with the nature of the liquid in which the wire was immersed, its exact resistance was not determined. Under exactly comparable conditions this variation of the resistance is linear when plotted against the temperature.

The Ammeter.—A potentiometer, a resistance of 0.1 ohm capable of carrying 15 amperes without heating, and a Weston standard cell, all furnished by the Leeds & Northrup Co., and all checked by the Bureau of Standards, were used to measure the current. The units used were the International ohm and the value of the Clark cell at 15° C = 1.434 volts. A sensitive galvanometer furnished by Keiser and Schmidt was used in obtaining a balance and the combination worked perfectly. The current was obtained from storage batteries giving about 24 volts, and was regulated and held exactly constant during the experiment by means of slide wire resistances, usually of 11 ohms and of 90 ohms, placed in parallel. Approximate regulation before each experiment was made with the 11 ohm resistance, and exact regulation completed in a few seconds after the current was finally turned on for the experiment by use of the 90 ohm coil.

The Voltmeter.—The drop in voltage across the terminals of the platinum coil was obtained by means of a Weston Laboratory Standard Voltmeter. The voltmeter was frequently checked by use of the potentiometer, standard cell, etc., above mentioned. At no time did the voltmeter give absolute readings, the corrections, amounting usually to about 0.5 of one percent, being obtained from a curve constructed from the check readings above mentioned. The re-

sistance coil of the instrument corresponding to the 15 volt scale had a resistance of 2606.3 ohms and required no correction for temperature. The 3 volt scale sometimes used had a resistance of 521.26 ohms and a temperature coefficient of $\alpha = 0.00035 (t - 22.5^\circ)$. A correction was made for the shunt current through the instrument.

The Time.—The time was measured by means of a small laboratory clock that struck each minute. Such a clock enables the current to be switched on and off, and the voltmeter and thermometer readings to be taken, at precisely the right moment, and is an indispensable part of the equipment for such work. It was compared with a clock giving standard time.

The Energy Added.—The calorie from 15° to 16°C is taken as equal to 41.88×10^6 ergs.¹ The total energy added is therefore equal to

$$1. \quad 0.2388 \times \text{Time in seconds} \times \text{Average corrected drop in voltage} \times \text{Corrected amperes, calories.}$$

In obtaining the average corrected drop in voltage, if the experiment lasts n minutes, and $E_0, E_1, E_2, \dots, E_n$, are the corrected voltmeter readings, then,

$$2. \quad E_{\text{average}} = \frac{\frac{E_0 + E_n}{2} + E_1 + E_2 + \dots + E_{n-1}}{n}.$$

The Thermometers.—Two thermometers, reading from -12° to 56° and from 32° to 70° in $1/10$ of a degree, were used during the experiments. Corrections for the thermometers were certified by the Reichsanstalt. With the aid of a magnifying glass the thermometers could be read to 0.01° . Corrections for the exposed stem were made in the usual manner. Later the determinations were checked at low and at high temperatures by use of a Beckmann thermometer of the usual construction. The corrections necessary to

¹ Ber. phys. Ges., 6, 578. Rowland, corrected by Day: Phys. Rev., 6, 194 (1898).

reduce to a hydrogen thermometer for the scale of this thermometer at different settings were furnished by the Bureau of Standards.

Heat Loss from the Calorimeter.—To obtain the necessary corrections for the loss or gain of heat from the calorimeter the thermometer was read for a sufficient time, usually 20 or 30 minutes, both before and after the experiment. The continued readings largely eliminated individual errors in the reading of the thermometer. The rates of cooling (or heating) obtained from the experiments with water and with benzol were plotted and it was found that the flask obeyed Newton's law of cooling with considerable accuracy even when a difference in temperature of 40° existed between the flask and the surrounding air. The fall in temperature per minute per degree difference of temperature between the flask and the surrounding air was found to be about 0.00043 for water and 0.000108 for benzol. Thus the flask was a remarkably efficient calorimeter.

The corrections for the loss or gain of heat by the flask can be accurately and simply made if the calorimeter rises evenly in temperature¹ from the beginning to the end of the experiment. Let θ_o and θ_n be the corrected temperatures at the beginning and at the end of the experiment respectively. Suppose that the experiment lasted n minutes and that v_o and v_n represent the rate of cooling before and after the experiment. Then Newton's law being true, and the above condition as to the addition of heat being fulfilled, it is easily shown that the total rise of temperature of the calorimeter is,

$$3. \quad \theta_n - \theta_o + \frac{n}{2} (v_o + v_n).$$

The "temperature before" ($= \theta_o \pm \frac{n}{2} v_o$) and "temperature after" ($= \theta_n \pm \frac{n}{2} v_n$), the experiment given in Tables 2 and 3, have been corrected for the heat lost by radiation.

¹ See page 805.

The Lag of the Thermometer.—The lag of the thermometer itself behind the true temperature of the immediately surrounding liquid is entirely negligible. The method of determining this lag, and its effect, has been recently discussed several times.¹ The lag of any thermometer is usually equal to the rate of cooling of the calorimeter divided by the cooling constant b of the thermometer. This cooling constant is obtained on heating the thermometer and plunging it into a bath of constant temperature and noting the cooling curve of the thermometer. The equation of this cooling curve is, from Newton's law of cooling,

$$4. \quad \frac{d\theta}{dt} = b\theta.$$

Now the experiments of Richards, Henderson and Forbes, and of Jäger and v. Steinwehr show that for a Beckmann thermometer b is quite variable but may be estimated as between 4 and 11. If therefore we suppose a rise in temperature of 10° during an experiment, the difference in the lag of the thermometer before and after the experiment, taking b equal to 4, would be 0.0027° with benzol and 0.0011° with water. Even with benzol the error is only $1/4000$ of the total rise in temperature. In reality the error is less than this, for the bulb of the thermometer used was small, and while b was not determined, it could hardly have been so small as 4.

It must be noted that the above discussion of the thermometric lag supposes that no heat is lost along the stem of the thermometer. Now it is quite possible to imagine with the very efficient Dewar flask above described that the heat of the water in the calorimeter will escape faster along the thermometer stem than it does through the vacuum

¹ M. Thiesen: *Metron Beitr.* (Normal Eichungskommission), 3, 13 (1881). J. Hartmann: *Zeit. Instrumentkunde*, 17, 14 (1897). F. M. Jäger and H. von Steinwehr: *Verhandl. deutsch. phys. Ges.*, 5, 50, 353 (1903). *Zeit. phys. Chem.*, 53, 153 (1905); 54, 428 (1906). T. W. Richards and A. B. Lamb: *Proc. Am. Acad.*, 40, 659 (1904-05). T. W. Richards, L. J. Henderson and G. S. Forbes: *Ibid.*, 41, 1 (1905-06). W. P. White: *Phys. Rev.*, 27, 526 (1908); 28, 462 (1909).

silvered walls of the vessel. In this case the thermometer would not only not lag behind the temperature of the calorimeter when it is cooling but would actually indicate a temperature lower than that of the liquid in the calorimeter. Yet even under such circumstances the above-described method would of course show a positive thermometric lag, the true lag in this case being negative.

In conclusion it may safely be said that unless the work requires an accuracy greater than 1 part in 4000 the lag of the thermometer itself may be neglected.

Difference of Temperature within the Calorimeter. Stirring.

—The temperature of the platinum wire itself when immersed in a liquid and carrying a current rises above that of the surrounding liquid. If the thermometer is placed in the immediate neighborhood of the wire coil the temperature as indicated by the thermometer will be found to rise regularly at a very nearly constant rate during the experiment. This was determined from observations upon many experiments. The thermometer does not, however, indicate the average temperature of the liquid because this temperature is greatest at the platinum coil and decreases with the distance from the coil. If the bulb of the thermometer is in the immediate neighborhood of the coil, the thermometer indicates always a temperature above the average temperature of the entire liquid. The outside layers of the liquid, which really determine the radiation loss, are at a lower temperature than the average temperature of the liquid. Efficient stirring would tend greatly to diminish these inequalities in temperature. *Yet such stirring, under the conditions of the experiments detailed, contrary to the usual idea, is not a matter of necessity even for accurate work.* For within a minute after the electric current is turned on currents are set up in the liquid which cause it to circulate. When these currents have been once established the circulation is fairly rapid, the rapidity depending on the liquid and on the size of the current used. These currents were observed in a similar single-walled flask by means of suspended material placed in the flask. With

water as the liquid, and a current of 5 amperes giving a rise in temperature of about one degree per minute, the circulation when established caused the water to rise from the bottom to the top of the flask in less than 15 seconds. Suppose, however, that the outside layer of water lags behind the true average temperature of the water by so much as 1° , equivalent to one minute. Then for an experiment lasting 10 minutes, with a rise of 10° in temperature, the error caused by the lag would be 0.0043, or an error of approximately $1/2500$. When one considers that this difficulty (inequalities of temperature within the liquid) could not be wholly eliminated by stirring, that an allowance, usually uncertain, must be made for the heat added by stirring, and that the stirring apparatus must be so constructed as to prevent evaporation from the flask (otherwise more serious errors are introduced), the proposal that we have made to eliminate the stirring should certainly meet with favor. Immediately after the end of the experiment the electric wires are disconnected and the flask thoroughly shaken. This shaking is repeated at intervals before each reading of the thermometer. Similarly of course the flask should be shaken before the experiment.

We have hitherto regarded the heat as being evenly added to the calorimeter. Since the current is kept constant, the heat added varies as the resistance, which increases by about $1/400$ of its value per degree. Could the entire contents of the calorimeter be kept precisely at its proper average temperature it would be practicable to allow for this increase of the resistance. The correction would amount usually to not more than 0.0001° and is of opposite sign to the more serious error caused by the lag of the liquid above mentioned. Hence it may safely be neglected.

The Calorimeter Constant.—The details of the experiments to determine the calorimeter constant given in the table below will be readily understood. The "Correction for vaporization" is a correction for the vaporization of the water into the neck of the flask, an empty space of about 60 cc ex-

isting there. The values used for the specific heat of water are based on the values given by Barnes and Cooke¹ based on the hydrogen thermometer, the International ohm, and the Clark cell at 15° C as equal to 1.4342 International volts. The water used was distilled and freshly boiled to free from dissolved air. The weight of the water was corrected for the buoyancy of the air, and allowance was made for the inequality in the length of the balance arms.

Experiments 15 to 19 inclusive were made with a Beckmann thermometer. In experiment 15, 16 and 17, the Beckmann was set at 5.95° and no bath was used. In experiments 18 and 19 the Beckmann was set at 60.02° and the calorimeter was surrounded by a bath kept at 56°.

Experiment 9 was a failure, due to an error in the thermometer reading and the details are omitted. On plotting the results of the experiments 1 to 14, it will be seen that they lie with great exactness on a line curved at its upper end, with the exception of experiments 5, 6, 11 and 14. Experiment 6 followed experiment 5 and it is pretty clear that an error must have been made in determining the intervening temperature change. In experiment 11 the voltmeter readings were irregular. We could not locate the error in experiment 14, nor in experiment 15 with the Beckmann thermometer.

A line through the results given will, we think, establish the calorimeter constant to within 0.3 of a calorie. This involves an accuracy of about one part in 1500 in the measurements directly concerned. Wherever in later experiments the Beckmann thermometer was used, the calorimeter constant, determined with its aid under the same conditions, was also used.

The Purity of the Benzol Used.—Kahlbaum's best thio-
phene free benzol was fractionated over a little phosphorus pentoxide through a Young's fractionating column of eight divisions until a constant boiling point was obtained. The

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¹ Phys. Rev., 15, 71 (1902).

TABLE I—Calorimeter constant

	Number of experiment									
	1	2	3	4	5	6	7	8	10	
Volts	6.9492	7.1182	6.3582	6.4945	6.6500	6.8102	6.9905	7.1385	6.4915	
Amperes	4.9974	4.9973	4.9976	4.9975	4.9975	4.9974	4.9974	4.9973	4.9975	
Time in minutes	10	10	10	10	10	10	10	8	10	
Total calories added	4975.8	5096.7	4552.8	4650.3	4761.7	4876.3	5005.4	4089.0	4648.2	
Correction for vaporization	1.5	2.1	0.3	0.3	0.7	0.9	1.7	2.3	0.3	
Temperature before	46.974	57.261	8.386	18.482	28.534	38.598	49.224	59.425	18.520	
Temperature after	57.613	68.103	18.166	28.481	38.731	49.085	59.930	68.137	28.517	
Δt	10.639	10.842	9.780	9.999	10.197	10.487	10.706	8.712	9.997	
Average temperature	52.29	62.68	13.28	23.48	33.63	43.84	54.58	63.78	23.52	
Calories added per degree	467.56	469.90	465.50	464.95	466.90	464.90	467.38	469.09	464.93	
Weight of water	452.65	452.65	452.08	452.08	452.08	452.08	452.08	452.08	452.06	
Specific heat of water	0.9982	0.9994	1.0009	0.9983	0.9974	0.9975	0.9984	0.9995	0.9983	
Total heat of water	451.84	452.38	452.49	451.32	450.91	450.95	451.28	451.86	451.29	
Calorimeter constant	15.72	17.52	13.01	13.63	15.99	13.95	16.10	17.23	13.64	

TABLE I.—Calorimeter constant (Continued)

	#									
	Number of experiment									
	11	12	13	14	15	16	17	18	19	
Volts	6.6380	6.7975	6.9622	7.1257	5.0520	5.0385	5.0416	5.6546	5.6522	
Amperes	4.9975	4.9974	4.9974	4.9973	3.9980	3.9980	3.9980	3.9978	3.9978	
Time in minutes	10	10	10	10	8	9	7	7	9	
Total calories added	4753.1	4867.2	4985.1	5102.1	2315.2	2597.6	2021.6	2267.2	2913.8	
Correction for vaporization	0.7	0.9	1.6	2.3	0.1	0.1	0.1	1.1	1.4	
Temperature before	27.693	37.715	47.475	57.762	1.096	0.293	1.683	1.138	0.227	
Temperature after	37.895	48.155	58.139	68.600	6.046	5.888	6.021	5.991	6.456	
Δt	10.202	10.440	10.664	10.838	4.950	5.595	4.338	4.853	6.229	
Average temperature	32.80	42.93	52.81	63.18	9.52	9.04	9.80	63.58	63.36	
Calories added per degree	465.83	466.10	467.32	470.55	467.65	464.26	466.02	466.95	467.55	
Weight of water	452.06	452.06	452.06	452.06	449.85	448.53	450.09	449.51	450.93	
Specific heat of water	0.9974	0.9975	0.9983	0.9995	1.0026	1.0028	1.0025	0.9995	0.9995	
Total heat of water	450.89	450.94	451.29	451.84	451.01	449.78	451.21	449.29	450.71	
Calorimeter constant	14.94	15.16	16.03	18.71	16.64	14.48	14.81	17.66	16.84	

sample finally used showed a boiling point of 79.49° to 79.55° , the barometer varying meanwhile from 747.7 to 748.3. This was equivalent to a boiling point of 80.02° to 80.05° at 760 millimeters pressure.

The Specific Heat of Benzol.—The details of the determination of the specific heat of benzol are given in Table 2 below. The weight of the benzol given is corrected for the buoyancy of the air and for the inequality of the balance arms. Experiments 1 to 5 were consecutive experiments, and the results lie on a straight line nearly parallel to and somewhat below the results of the similar experiments 5 to 11. Therefore the specific heat of the benzol was determined both at high and at low temperatures with the Beckmann thermometer as detailed in experiments 12 to 15. The setting of the Beckmann in experiments 12 and 13 was at 5.95° and no bath was used. In experiments 14 and 15 the Beckmann was set at 60.02° and the calorimeter was kept in a bath at about 59.5° . The calorimeter constant determined with the Beckmann under similar conditions was used. The results of the check experiments show that the series of experiments 6 to 11 are correct, though we could never locate the exact trouble with the series 1 to 5.

The specific heat of benzol may therefore be taken as lying on a straight line passing through the points 0.3971 at 0° and 0.4369 at 70° . This line is shown in Figure 1, line 12, and the values at intervals of 10° taken from this line are given in Table 3. The values given do not agree with any previous measurement. We believe, however, that the results given are correct to within 1 part in 200.

The Specific Heat of the Saturated Vapor.—The heats of vaporization of benzol at intervals of 10° obtained by three different methods are given in Table 3 below.

The values in the column headed "Griffiths and Marshall" are from the formula, latent heat = $107.05 - 0.1581t$, obtained from the very accurate experiments¹ made by these workers at 20° , 30° , 40° and 50° .

¹ Phil. Mag., 41 (1896).

TABLE 2—Specific heat of benzol

	Number of experiment								
	1	2	3	4	5	6	7	8	9
Volts	3.8314	3.9490	4.0577	4.1542	4.2435	3.7950	3.9000	4.0053	4.0975
Ampères	2.9985	2.9985	2.9984	2.9984	2.9984	2.9986	2.9985	2.9985	2.9984
Time in minutes	10	12	10	10	10	10	11	10	10
Total calories added	1646.1	2035.9	1743.2	1784.7	1823.0	1630.5	1843.1	1720.8	1760.3
Correction for vaporization	0.9	1.1	1.4	2.0	2.2	0.8	1.0	1.6	2.0
Temperature before	9.280	19.261	30.858	40.261	49.043	9.184	18.946	29.441	38.699
Temperature after	18.880	30.899	40.680	50.134	59.007	18.586	29.404	39.017	48.398
Δt	9.600	11.638	9.822	9.873	9.964	9.402	10.458	9.576	9.699
Average temperature	14.08	25.08	35.77	45.20	54.02	13.88	24.17	34.23	43.55
Calories added per degree	171.38	174.84	177.34	180.56	182.74	173.33	176.14	179.53	181.28
Calorimeter constant	12.93	13.79	14.60	15.30	16.07	12.92	13.70	14.48	15.20
Weight of benzol	393.12	393.12	393.12	393.12	393.12	395.19	395.19	395.19	395.19
Specific heat of benzol	0.4031	0.4096	0.4139	0.4204	0.4240	0.4059	0.4110	0.4176	0.4203

TABLE 2—Specific heat of benzol (*Continued*)

	Number of experiment					
	10	11	12	13	14	15
Volts	4.1839	4.2835	2.4789	2.4805	4.2945	2.8117
Amperes	2.9984	2.9984	1.9952	1.9952	2.9984	1.9946
Time in minutes	11	10	12	11	5	13
Total calories added	1977.2	1840.2	850.38	780.00	922.49	1044.61
Correction for vaporization	2.5	3.3	0.35	0.32	1.92	2.21
Temperature before	46.958	56.550	1.376	1.449	—0.013	—0.098
Temperature after	57.605	66.332	6.279	5.941	4.880	5.477
Δt	10.647	9.782	4.903	4.492	4.893	5.575
Average temperature	52.28	61.44	9.77	9.64	62.45	62.71
Calories added per degree	185.47	187.78	173.41	173.57	188.14	186.98
Calorimeter constant	15.85	17.05	14.67	14.64	17.20	17.22
Weight of benzol	395.19	395.19	394.38	395.20	393.87	393.08
Specific heat of benzol	0.4292	0.4320	0.4025	0.4022	0.4340	0.4319

The values in the column headed "Ther." are calculated from the data given by use of the well-known Clausius-Clapeyron thermodynamical equation

$$5. \quad L = 0.043183 T \frac{dP}{dT} (V - v) \text{ calories,}$$

where L is the heat of vaporization, T is absolute temperature, P is pressure in millimeters of mercury, and v and V are the volumes of a gram of the liquid and of its saturated vapor. The vapor pressure, density and volume of the liquid, and density and volume of the vapor at 70° are from observations by Young.¹ The density and volume of the vapor at 0°C are the theoretical values calculated on the supposition that the vapor behaves as a perfect gas at this temperature, a supposition that must be very nearly correct. The equation used for calculating the density is

$$6. \quad D = 0.0416014 \frac{Pm}{T},$$

where m is the molecular weight and is equal to 78.05. The densities of the saturated vapor at 10° to 60° inclusive are obtained by extrapolating the equation given by Young.² This extrapolation gives results that cannot be far wrong since the theoretical densities serve as a guide to which the actual densities must approach as a limit.

The values of the heat of vaporization in the column headed "Mills" are obtained by using the equation

$$7. \quad L = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) + E_e.$$

Here μ' is a constant for any particular substance and for benzol has the value 109.26. E_e is the energy expended in overcoming the external pressure as the liquid expands to the volume of the saturated vapor and is given by the equation

$$8. \quad E_e = 0.043183 P(V - v) \text{ calories.}$$

The values of E_e given in Table 3 have been slightly smoothed.

¹ Sci. Proc. Roy. Dublin Soc., 12, 374 (1910).

² Jour. Phys., Jan. (1909).

Equation 7 has been carefully and extensively studied¹ and seems to hold accurately for non-associated liquids at all temperatures.

Making use of these values of the heats of vaporization and the values of the specific heat of the liquid, it becomes possible to calculate the specific heat of the saturated vapor, for the energy necessary to change the liquid at 0° into the saturated vapor at 10° is the same whatever may be the method pursued to effect the change. Letting the subscripts denote temperature, and letting σ_L denote the total heat added to the liquid and σ_v that added to the vapor between the temperature limits given, we have,

$$9. \quad L_0 + \sigma_v = L_{10} + \sigma_L, \text{ or } \sigma_v = L_{10} + \sigma_L - L_0.$$

It should be understood that the method here used for obtaining the specific heat of the saturated vapor involves no assumption beyond the law of the conservation of energy, the values of the specific heat of the liquid and of the heat of vaporization being known.

The specific heat of the saturated vapor so calculated from the values of the heat of vaporization given by Griffiths and Marshall will lie, as can readily be seen, on a straight line, parallel to and 0.1581 below, the line giving the specific heat of the liquid. The values are given in Table 3. It is probable that the heat of vaporization, even at this low temperature (0° to 70°), does not vary exactly linearly with the temperature, and we think too much faith should not be placed in the values so derived.

Unfortunately the specific heats of the saturated vapor derived from the thermodynamically calculated heats of vaporization are even worse. The average values are given every 10° from 5° in Table 3. They defy smoothing. The thermodynamically calculated heats of vaporization are fairly accurate as can be seen from the extended data given

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¹ Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905), 10, 1 (1906); 11, 132, 594 (1907); 13, 512 (1909). Jour. Am. Chem. Soc., 31, 1099 (1909).

TABLE 3—The specific heat of the saturated vapor of benzol

Tem- pera- ture	Vapor pressure P	Density of liquid d	Volume of liquid v	Density of vapor D	Volume of vapor V	External energy E_e	$\bar{v}_d$	$\bar{v}_D$	$\bar{v}_d - \bar{v}_D$	Specific heat of liquid σ
0 ¹	26.54	0.9001	1.1110	0.0 ₃ 1215	8230	6.94	0.9655	0.04953	0.91597	0.3970
10	45.43	0.8894	1.1243	0.0 ₃ 2024	4939	7.17	0.9617	0.05872	0.90298	0.4027
20	74.66	0.8789	1.1378	0.0 ₃ 3208	3117	7.41	0.9579	0.06845	0.88945	0.4084
30	118.24	0.8685	1.1514	0.0 ₃ 4911	2036	7.65	0.9541	0.07890	0.8752	0.4141
40	181.08	0.8575	1.1661	0.0 ₃ 7290	1372	7.89	0.9500	0.09000	0.8600	0.4298
50	268.97	0.8466	1.1812	0.001052	950.6	8.13	0.9460	0.10170	0.8443	0.4255
60	388.58	0.8357	1.1966	0.001479	676.1	8.36	0.9419	0.11395	0.82795	0.4312
70	547.40	0.8248	1.2124	0.002040	490.3	8.52	0.9378	0.12682	0.81098	0.4369
Tempera- ture	Heat of vaporization				Specific heat of saturated vapor					
	Griffiths and Marshall	Ther.	Mills	Griffiths and Marshall	Mills smoothed	Average for 10° at	Ther.	Mills		
0 ¹	107.05	106.11	107.02	0.2389	0.284	5	0.2258	0.2808		
10	105.47	104.37	105.83	0.2446	0.282	15	0.3315	0.2815		
20	103.89	103.63	104.59	0.2503	0.279	25	0.3122	0.2792		
30	102.31	102.64	103.27	0.2560	0.277	35	0.3075	0.2749		
40	100.73	101.55	101.85	0.2717	0.275	45	0.2806	0.2756		
50	99.14	100.13	100.38	0.2674	0.273	55	0.2823	0.2723		
60	97.56	98.67	98.82	0.2731	0.270	65	0.2370	0.2650		
70	95.98	96.70	97.13	0.2788	0.268	—	—	—		

¹ Benzol is a solid at 5.43°. The lines for the liquid are extrapolated to 0° for convenience.

in the papers cited, probably seldom diverging from the true value by so much as one calorie. But this comparatively small error is proportionately enormously magnified when the differential of the latent heat is the important factor. Measurements over a wider range of temperature are necessary before one could undertake to smooth out the effect of the individual errors of observation.

The specific heat of the saturated vapor calculated from the heats of vaporization under the heading "Mills," given by equation 7, are given at intervals of 5° in Table 3 and the smoothed values are also there given. We are inclined to believe that these smoothed values for the specific heat of the saturated vapor of benzol are fairly accurate. Observations over a wider range of temperature are, however, necessary before the values can be finally accepted.

The object of this research was to throw light upon the nature and cause of the energy changes involved during the rise in temperature of a liquid. Theoretical discussion of the results is postponed to a later paper.

Summary

1. A method for determining accurately the specific heat of a liquid at temperatures below its boiling point is described in detail. The method uses a 500 cc Dewar flask as a calorimeter and electrical heating of the liquid.

2. The specific heat of liquid benzol is found to vary linearly with the temperature between its freezing point and 70°C . The line passes through the values 0.3970 at 0° and 0.4369 at 70°C .

3. The specific heat of the saturated vapor of benzol has been determined, though further work is necessary to confirm the results obtained. The values tentatively given lie on a straight line passing through the values 0.284 at 0° and 0.268 at 70°C .

The above work was done in the Chemical Laboratory of the University of North Carolina.

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