deuteride are approximately twice as great as those of sodium hydride.

3. The following heats of formation per mole have been calculated: for sodium hydride, 14,440 calories; for sodium deuteride, 15,800 calories.

BRYN MAWR, PENNA. RECEIVED OCTOBER 25, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

A Semi-micro Calorimeter for Measuring Heat Capacities at Low Temperatures[1]

BY DANIEL R. STULL

In view of the trend toward micro and semi-micro apparatus it seemed to be of interest to construct a calorimeter for small amounts of organic liquids which would enable measurements of specific heats and heats of transition to be made in the range 100 to 320°K. The calibrated heat conductivity calorimeter developed by Andrews,[2] Haworth,[3] and Smith,[4] was selected as the basis for the experiments.

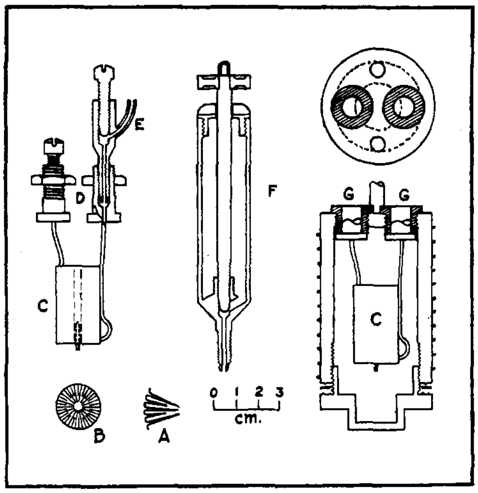

Fig. 1.

Calorimeter Construction

A pilot calorimeter was first built which was used to try out several ideas of design and construction.[5] With the experience obtained on this calorimeter as a guide, the apparatus was constructed in its final form as follows: a can with vanes inside was formed by bending a strip of gold 0.05 mm. thick, 3.5 cm. wide and nearly a meter long as shown in the end view at A and B of Fig. 1. To add strength the outside was plated with copper, and the ends were closed by plated copper, thus producing a container possessing no joints or fissures. In this way the vanes were an integral part of the can.

Entrance and exit tubes of 1-mm. German silver tubing were soldered in place (shown at C) and also a thermocouple well reaching up 1 cm. from the bottom of the can. In order to simulate "black body" conditions better the can was plated finally with a fine grained spongy layer of copper, washed and dried, and placed in a 110° oven for three hours, thereby converting the surface to a velvet black copper oxide.

After the plating was completed, the entrance and exit tubes were soldered to brass bushings D threaded in the manner shown. The screws had spherical ends which made gas and liquid tight valves when in contact with the conical seats of the bushings. The brass fitting E was designed to permit control of the gas and liquids which were passed through the can for cleaning purposes.

At F is shown the brass container in which the liquids under investigation were weighed. It was threaded to fit the bushing D and contained a sphere-cone valve in the bottom. After the sample had been weighed in this container, it was inserted into the bushing D and the valve opened to permit the sample to drain by gravity into the can. The opposite bushing valve which had been serving as a vent and the valve in the weighing container were then closed and, after withdrawal from the bushing, the former was reweighed. The amount clinging to the tip was found to be negligible. Independent preliminary transfers showed that the difference between the weight lost by the weighing container and that gained by the receiver averaged less than 0.1% on a 5-g. sample of benzene. The total volume of the can was about 6 ml. although the samples taken in most of the work were about 3 to 3.5 ml.

The shield was of copper 5.2 cm. in diameter, 7.5 cm. long with a wall thickness of 6.5 mm. (see Fig. 1). The bottom was closed by a threaded copper plug and made gas tight with a lead gasket. In addition the joint was finally sealed with low melting solder. The inside of the shield was given a velvet black surface similar to that of the can. The top of the can was pierced by four holes. Into the two smaller were soldered 6.5-mm. German silver tubes, one carrying the thermocouple wires and the other providing gas connection with the outside. The can was suspended in the shield by the bushings D (Fig. 1) which were secured in the hard rubber plugs G and bakelited in position. This was necessary for electrical insulation. Twenty ohms of no. 30 constantan wire was bakelited on the outside of the shield as a heater.

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[1] Part of a dissertation presented to the Faculty of Philosophy of The Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] D. H. Andrews, THIS JOURNAL, **48**, 1287 (1926).

[3] E. Haworth and D. H. Andrews, *ibid.*, **50**, 2998 (1928).

[4] R. H. Smith and D. H. Andrews, *ibid.*, **53**, 3644 (1931).

[5] It was with this apparatus that the data cited by R. C. Lord, Jr., and E. R. Blanchard, *J. Chem. Phys.*, **4**, 707 (1936), were obtained.

The thermocouples were made of no. 40 double silk covered copper wire and no. 30 constantan wire d. s. c. coated with bakelite and baked. The constantan wire came from the spool used by Southard and Andrews[6] in preparing their thermocouple tables. It was tested for homogeneity in the usual way.[7] The couples were then compared carefully with a platinum resistance thermometer[8] and it was found that they checked Southard's values to better than 0.05° over the range 90.1 to 310.2°K., and checked those of Smith[9] to 0.1°.

After the calorimeter had been assembled, melting points of carefully purified substances were determined, confirming the calibration of the thermocouples. Table I shows the melting point data of these substances.

A thermocouple and two constantan wires were soldered to the bottom of the thermocouple well. The other two ends of these constantan wires were combined with two other couples, and soldered one to each side of the shield (see Fig. 1). The thermocouple wires were led out one of the German silver tubes at G (Fig. 1) through a de Khotinsky seal to the outside. The ice junctions were singly coated with bakelite and baked to insulate them from each other.

The electrical circuits are shown in Fig. 2. The thermocouple leads were connected to a double pole double throw switch H and their e. m. f. read with a Type K potentiometer A. In the diagram the solid lines represent copper wires, and the dotted lines represent constantan wires. The two copper leads from inside the calorimeter were connected to a Type K potentiometer B on which could be measured any e. m. f. due to a temperature gradient between the can and shield. The potentiometers were connected to high sensitivity galvanometers.

In order to maintain a constant potential difference between the thermouples on the can and on the shield, the beam of light from the galvanometer B was arranged so that when deflected from its zero position, it was reflected from a mirror M into a photoelectric relay. A clock-operated pendulum with a period of about one second was placed so that at the end of its stroke it cut the light beam for a small fraction of a second. This reduced the "off and on" lag of the relay very considerably as explained later.

The heater on the shield (20 ohms) was connected in series with eight 6-volt storage batteries, with an ammeter, with 12 ohms variable resistance which was by-passed by the photoelectric relay, and with 1500 ohms variable resistance (see Fig. 2).

The other German silver tube out of the top of the shield led to a phosphorus pentoxide trap and a soda lime trap, thence to a reservoir of 40-liter capacity into which pure nitrogen was fed, and which was maintained at a pressure 10 mm. higher than atmospheric by a mercury bubbler. This was done so that if any leaks should develop the flow of gas would be outward, avoiding contamination by oxygen, water vapor, or carbon dioxide. Before filling the whole system was pumped out several times, each time refilling with nitrogen.

The shield itself was suspended by the two German silver tubes from a brass plate and was just the right length to reach to the bottom of a 1-liter wide-mouthed Dewar flask. The bottom of the plate carried a large cork which fitted the Dewar flask, and helped to minimize the heat leak.

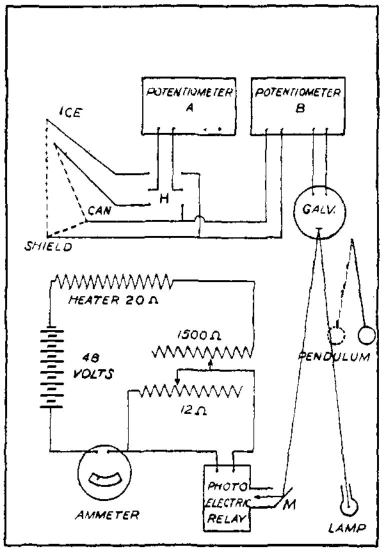

Fig. 2.

Experimental Procedure

The principle of the method may be stated briefly as follows: if heat is radiated and conducted from the shield to the can at a constant rate, the time necessary to heat through a given temperature interval will be proportional to the average specific heat of the can and its contents over that temperature interval.

After having introduced the sample in the manner previously mentioned, the valves were closed, and a wide-mouthed 1-liter Dewar flask containing about 400 ml. of liquid nitrogen was brought up around the shield and left there until thermal equilibrium was reached. The Dewar was then removed, and a similar Dewar (room temperature) was placed around the shield and remained there throughout the rest of the run.

The heater was started and adjusted so that a thermal head of 400 μv. was established and maintained. By careful adjustment of the two resistances, the thermal head could be maintained constant to about 0.25%. Similar automatic controls of temperature have been described by Southard and Andrews,[6] and by Scott and Brickwedde.[10]

There is a lag, however, in the operation of photoelectric cell relays. For example, for the relay to engage, the field of the photoelectric cell must be, let us say, 80% illuminated, but once engaged, the relay *stays* engaged until the photoelectric cell is only 20% illuminated. This lag can be largely overcome if the light beam is periodically broken, *i. e.*, made to go to zero illumination

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(6) Southard and Andrews, *J. Franklin Inst.*, **207**, 329 (1929).

(7) White, THIS JOURNAL, **36**, 2292 (1914).

(8) NBS No. 499, calibrated at the National Bureau of Standards, May 20, 1936, Test No. 76559.

(9) Dissertation of R. H. Smith, The Johns Hopkins University, 1930, p. 37.

(10) Scott and Brickwedde, *Bur. Standards J. Research*, **6**, 407 (1931).

for a small fraction of a second. To do this, a clock-actuated pendulum was placed so that it spent a very short time in the beam at the end of its swing. Thus the relay was disengaged once a second, and if the illumination fell to say 75%, the relay would not reëngage until the illumination reached the 80% value again. In this way the thermal head could be kept constant to about 0.1%. This represents the uncertainty of the average difference over the time interval between two calorimeter temperature readings.

After the thermal head was established, and had become steady, the A potentiometer was set at a given temperature say 85.0°K. (−5300 μv.). As the can and contents heated up, the A galvanometer slowly drifted across the scale. When the can had warmed to exactly 85.0°K. the galvanometer was at its zero point, and a stopwatch was started. *Immediately* thereafter the *A* potentiometer was reset at 96.6°K. (−5100 μv.), and as the galvanometer beam crossed the zero point again, the first stopwatch was stopped and another started. Thus at this point the temperature interval was 200 μv., and the average temperature, Θ, for the interval was 91.0°K. (−5200 μv.). This procedure was repeated every 200 μv., until a point of transition was reached. When this occurred, the apparent specific heat of the sample greatly increased. This meant that the heating current had to be decreased to keep the thermal head constant because the shield itself no longer absorbed heat. After the heat of transition had been absorbed, the regular heating was resumed, and the run continued until the desired temperature was reached for the end of the run. A time-temperature plot of the temperatures of the can through the transition point gave a very good determination of the melting or transition point.

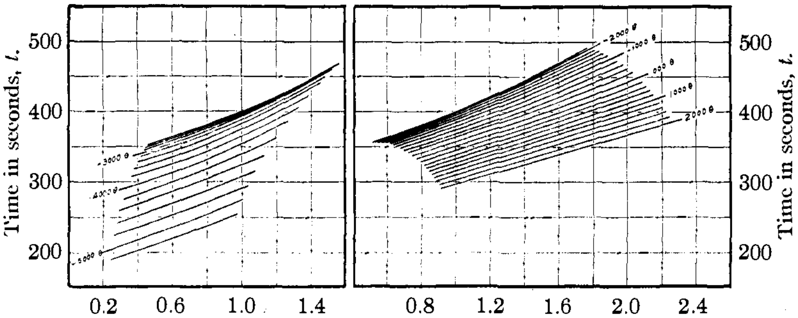

Fig. 3.

After every run the valves at the top of the shield were opened. Into the appropriate one was screwed the fitting E (Fig. 1) and into the other one was screwed the weighing container with valve open. Clean compressed air was passed in through E, thus forcing the liquid up into the weighing container. After the valve had been closed, the weighing bottle was removed, and the sample disposed of. A wash of a volatile solvent, usually benzene, was placed in the can and then removed. The can was cleaned by blowing through clean compressed air until two or three hours after the time when the exhaust carried no smell of the material last run in the can.

The main sources of error in this method are: the quantity of material, the time measurement, the temperature measurement, the thermal head adjustment, the temperature distribution over the shield, and that over the can. The delicacy of each of the first four has been calculated as one per mille or better. Little is known concerning the last two.

Calibration

The apparatus was calibrated by running different weights of benzene in the can. For this purpose it was necessary to know accurately the specific heat of benzene over the range 100 to 320°K. The specific heat data for benzene from the literature[11] were plotted and a best curve drawn. Points read from this curve were used in the calibration. Uniform points for comparison purposes will be found in Table II.

Ten runs were made with samples of benzene weighing from 2.6890 g. to 4.8730 g. (3.1 to 5.6 ml.). This gave ten values of time for every Θ. From the weight of the sample and the best benzene data there was calculated the specific heat of that sample, wc_p. A plot of time in seconds against wc_p in g. cal.$_{15}$ gave a series of nearly straight lines, one for each value of Θ (see Fig. 3). Thereafter a calibration run was made with benzene every two weeks or less. The results proved beyond a doubt that the original calibration was as valid at the last as it was at the first run.

As an independent check on the apparatus and method, toluene was studied, and its specific heat calculated. The results are shown in Fig. 4 and are compared with the toluene data of Kelley.[12] The greatest deviation in the solid state amounted to about 3% at 128.52°K., while in the liquid state the deviation amounted to 1% at 222.77° and 2% at 252.48°K. in two points that Kelley himself questioned. The value for the liquid state was about 1% lower at 300°K. than the results of Daniels and Williams.[11]

The procedure for studying substances for which the specific heat is not known is as follows. The experimental data for each run consisted of values of Θ differing by 200 μv., and running from −5200 to +2000 μv. along with the time in seconds required to warm through the 200 μv. interval. With the use of the calibration chart (Fig. 3) the time for any given temperature increment (Θ) could be converted to the proper wc_p value. This gave the average specific heat of the sample for that particular increment of temperature. Multiplication by the factor (weight of sample/molecular weight) gave the average specific heat per mole for that particular temperature range.

When a transition point was reached, the time necessary

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(11) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930); Maass and Waldbauer, *ibid.*, **47**, 7 (1925); Richards and Wallace, *ibid.*, **54**, 2705 (1932); Daniels and Williams, *ibid.*, **46**, 903 (1924); "International Critical Tables," Vol. V, pp. 103–115; Landolt–Börnstein–Roth–Scheel, "Physikalische-chemische Tabellen," J. Springer, Berlin, 1927, p. 692.

(12) Kelley, THIS JOURNAL, **51**, 2739 (1929).

to traverse that temperature increment would be very much greater. For example, to melt 5.39 g. (6.2 ml.) of benzene required 46 min. 30 sec. (2790 sec.), while the time required to heat the solid and liquid through the 200 μv. interval was 7 min. 30 sec. (450 sec.), making a grand total of 54 min. to traverse the 200 μv. interval.

By running the can empty its specific heat could be calculated. Totaling the specific heats of the can and its contents (here 5.39 g. of benzene) gave the heat absorbed in the 200 μv. interval (here 26.28 cal._{15}). This permitted calculation of the heat of fusion

$$\frac{2790}{450} \times \frac{26.28}{5.39} = \Delta H_f = 30.23\ \text{cal.}_{15}/\text{g.}$$

This value for the heat of fusion of benzene compares favorably with that of Huffman, Parks and Daniels,[11] 30.09 cal._{15}/g.

Materials

The benzene used in this work was J. T. Baker Chemical Co. special "Thiophene Free." It was recrystallized six times, discarding each time one quarter of the unfrozen liquid. It was placed over phosphorus pentoxide for two weeks, after which it was fractionated through a five-foot (152-cm.) column of Pyrex glass packed with small glass helices similar to those described by Young and Jasaitis.[13] The quantity collected for use boiled as shown in Table I. The purity was certainly above 99.95% on the basis of its melting point curves.

The toluene was obtained from Baker, dried over phosphorus pentoxide for two weeks and fractionated through the five-foot column. Its purity was above 99.90%.

The monohalogen benzenes were obtained from Eastman Kodak Co. and after fractionation through the five-foot column were collected at the temperatures stated in Table I. The iodobenzene when received showed an unmistakable pink tinge. After fractionation it was water white. Care was taken to keep it out of the light, and it remained water white. The purity of these was all above 99.9%.

The carbon tetrachloride was from Baker, and after two preliminary cuts in other stills in the Laboratory it was cut on the five-foot still. Its purity was well over 99.98%.

TABLE I

CRITICAL DATA FOR THE COMPOUNDS USED

Compound	$n^{20}\text{D}$	B. p., °K.	M.p., °K.
CS_2	1.628	319.45_{764}	161.59
CH_3OH	1.329	337.74_{764}	175.67
$CHCl_3$	1.446	334.27_{760}	209.61
CCl_4	1.461	349.85_{760}	250.37
C_6H_6	1.502	353.20_{760}	278.55
$C_6H_5CH_3$	1.496	383.70_{760}	177.89
C_6H_5F	1.465	357.89_{766}	231.10
C_6H_5Cl	1.525	405.25_{760}	227.89
C_6H_5Br	1.561	429.23_{768}	242.43
C_6H_5I	1.622	461.56_{768}	241.83
n-Hexane	1.375	341.78_{760}	177.90
2-Methylpentane	1.372	333.37_{760}	119.69
3-Methylpentane	1.377	336.36_{760}	......
2,3-Dimethylbutane	1.375	331.12_{760}	136.47
2,2-Dimethylbutane	1.369	322.90_{760}	172.13

The isomeric hexanes were synthesized by Cramer and Mulligan,[14] and after further purification by distillation in the General Motors Laboratory were sent to the National Bureau of Standards. The boiling points, dp/dT near the boiling point, and the freezing points were measured there by M. Wojciechowski. His data will be published later. He states that, according to measurements of the difference in boiling and condensation temperatures, these samples were very pure. Indeed the work done in this Laboratory on these isomeric hexanes fully substantiated this conclusion.

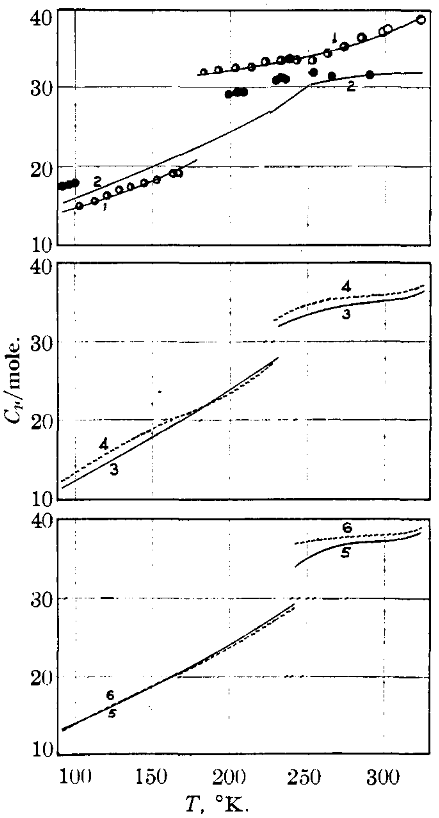

Fig. 4.—1, Toluene (◑, Kelly; ○, Daniels and Williams); 2, carbon tetrachloride, (●, Latimer); 3, fluorobenzene; 4, chlorobenzene; 5, bromobenzene; 6, iodobenzene.

Experimental Results

In view of the accuracy of the different measurements involved, the error in the results was placed at a maximum of 1.25% and in most cases probably was 0.75% or less. The heat of transition data were probably accurate to about 3%. All the work was expressed in terms of the defined calorie_{15}. (The factor 1.0004/4.185 has been used to convert international joules to the calorie_{15}.) All weights have been reduced to a vacuum basis.

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[13] Young and Jasaitis, THIS JOURNAL, **58**, 377 (1936).

[14] Cramer and Mulligan, *ibid.*, **58**, 373 (1936).

TABLE II

EXPERIMENTAL SPECIFIC HEAT DATA IN CALORIES$_{15}$ PER MOLE

T,°K.	C_6H_6	CCl_4	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I	*n*-Hexane	2-Methyl-pentane	3-Methyl-pentane	2,3-Dimethyl-butane	2,2-Dimethyl-butane
90	11.34	15.46	11.25	12.00	13.12	12.91	17.55	25.03	32.55		18.72
100	12.00	16.20	12.25	13.26	13.98	13.92	18.90	25.70	33.72		19.93
110	12.63	16.82	13.30	14.51	14.80	14.90	20.37	26.37	34.72		21.10
120	13.28	17.57	14.40	15.68	15.69	15.86	21.86	34.47	35.60		22.24
130	13.97	18.32	15.44	16.82	16.62	16.85	23.40	35.28	36.43		31.25
140	14.70	19.18	16.61	17.89	17.60	17.81	25.07	36.06	37.17	35.84	32.25
150	15.48	20.05	17.69	18.93	18.63	18.71	26.92	36.81	37.83	36.58	33.06
160	16.30	20.98	18.93	19.90	19.60	19.60	29.00	36.58	38.42	37.28	33.81
170	17.14	21.84	20.04	20.73	20.62	20.54	31.37	38.27	39.00	38.00	34.48
180	18.08	22.76	21.28	21.54	21.68	21.52	40.40	39.03	39.49	38.63	35.07
190	19.07	23.63	22.55	22.42	22.78	22.60	40.58	39.72	40.00	39.25	35.64
200	20.16	24.55	23.79	23.48	23.84	23.66	41.01	40.43	40.44	39.93	36.26
210	21.25	25.46	25.06	24.76	25.05	24.80	41.74	41.18	40.88	40.50	36.84
220	22.35	26.42	26.36	26.14	26.28	25.99	42.80	41.85	41.29	40.98	37.47
230	23.51	27.37	27.64	32.83	27.60	27.18	44.25	42.53	41.68	41.30	38.10
240	24.77	28.81	32.67	34.00	28.96	28.40	46.06	43.28	42.07	41.55	38.75
250	26.19	30.40	33.40	34.77	34.98	37.02	47.93	44.00	42.43	41.82	39.40
260	27.76	30.81	33.93	35.21	35.93	37.32	48.77	44.71	42.82	42.17	40.06
270	29.35	31.17	34.36	35.46	36.56	37.53	48.43	45.42	43.32	42.54	40.81
280	31.02	31.40	34.65	35.63	36.88	37.65	46.78	46.19	43.64	42.97	41.64
290	31.73	31.59	34.88	35.76	37.02	37.82	45.42	46.88	44.12	43.42	42.72
300	32.27	31.73	35.07	35.90	37.17	37.96	45.17	47.56	44.93	44.21	44.03
310	32.89	31.80	35.31	36.18	37.41	38.00	46.21	48.37	46.20	45.40	45.75
320	33.58	31.84	35.84	36.78	37.98	38.42	48.54	49.90	48.36	47.30	48.10

Over the temperature range 90 to 320°K. thirty-seven heat capacity determinations were made for each compound. These were plotted on a large scale, and a smooth curve drawn. The values found in Table II were read from this smooth curve. The heats of transition and fusion are given in Table III.

TABLE III

HEATS OF TRANSITION AND FUSION IN CAL.$_{15}$/MOLE

Compound	T,°K.	Heat (F = fusion) (T = transition)
Toluene	178.18	1560 F
Carbon tetrachloride	225.63	1100 T
	250.37	581 F
Fluorobenzene	231.10	2485 F
Chlorobenzene	227.89	2284 F
Bromobenzene	242.43	2540 F
Iodobenzene	241.83	2330 F
n-Hexane	177.90	2950 F
2-Methylpentane	119.69	89 F
2,3-Dimethylbutane	136.47	
2,2-Dimethylbutane	127.11	1095 T
	172.13	111 F

The objection may be raised that it would be more desirable to tabulate individual experimental points. Unfortunately the very nature of the method "smooths out" these points before they are in a form for significant tabulation. It was felt that the conversion of the data from the series of temperatures corresponding to equal increments in microvolts over to temperatures of equal increments in °K. did not alter the character of the results. Consequently the latter only are shown in the tables. An idea of the nature of these calculations may be obtained from the earlier papers on this type of calorimeter.[2-4]

The data on carbon tetrachloride cited by Lord and Blanchard[5] fell on a curve roughly about 0.8 cal. higher in the solid state than the data here presented, while the curve for the liquid state fell below the present work by more than a calorie at about 290°K. (see Fig. 4). The writer believes that the data obtained with the later calorimeter was more reliable. The data of Latimer[15] seemed to differ very considerably from that of this work. His points at 91.0, 95.0 and 99.5°K. fell over 12% above the curve (see Fig. 4), while his point at 199.5°K. was 20% higher. His points at 229.4 and 232.5°K. were over 13% above the curve while his point at 238.0°K. was about 17% higher. In the liquid state his points asymptotically approach the curve of the present work. The value of Mills and MacRae[16] at 273.1°K. agreed very

(15) Latimer, THIS JOURNAL, **44**, 90 (1922).

(16) Mills and MacRae, *J. Phys. Chem.*, **15**, 54 (1911).

well. The heat of transition value of 1100 cal.$_{15}$/mole agreed quite well with the value 1080.8 cal./mole of Johnston and Long.[17] The heat of fusion value of 581 cal.$_{15}$/mole also agreed well with their value of 577.2 cal./mole. The temperatures of these points agreed within 0.4°.

The literature data on the heat capacities of the monohalogen benzenes is quite sparse. The data of Andrews and Haworth[3] on phenyl chloride and bromide was consonant with the present work. The values in the solid state for the fluoride, chloride, bromide, and iodide all fell close to each other, and were quite similar. The values in the liquid state were nearly parallel and equally spaced one above the other with the fluoride on the bottom of the group and the iodide on the top (see Fig. 4). The values of the heats of fusion given by Timmermans[18] were not very consistent. His values are listed first followed by those of the present work. For fluorobenzene 1950 cal./mole against 2485 cal.$_{15}$/mole, chlorobenzene 1800 cal./mole compared with 2284 cal.$_{15}$/mole, and for bromobenzene 2000 cal./mole against 2540 cal.$_{15}$/mole.

The heat capacity data of the hexanes was confined to one of them—the normal. The literature contained two sets of data by Parks, Huffman, *et al.*[19,20] In the estimation of the author the data given last were more reliable. The data for the solid state were in fair agreement. At the lower end of the liquid state 183.5, 187.4, and 188.8°K. agreed very well, but then the points began to deviate until they reached a maximum of about 10% below the present work. This was because in the present work a "hump" was observed with a maximum of about 5.8 cal. in height at about 262.5° with "wings" extending symmetrically on both sides about 40° below and about 30° above (see Fig. 5). The heat of fusion for *n*-hexane was found to be 2950 cal.$_{15}$/mole, Parks, Huffman, *et al.*,[19,20] found 3110 and 3002 cal./mole, while Timmermans[21] found 3000 cal./mole.

The curves for the other isomeric hexanes will be found on Fig. 5. The 3-methylpentane showed no transition point over the whole range of measurements, and presumably formed a glass as has been suggested by Timmermans[22] for the 2-methylpentane. In the present investigation it was found that 2-methylpentane had a sharp definite melting point. An unusually low specific heat was observed for 2,3-dimethylbutane in the solid state. The work of Smittenberg, Hoog, and Henkes[22a] to appear in THIS JOURNAL showed that this hydrocarbon first freezes to give an α-modification at about 134°K. and then changes over to a β-modification at about 14° below this point. Sufficient time was not allowed for this transformation, and it masked the true specific heat, and led to the low results observed.

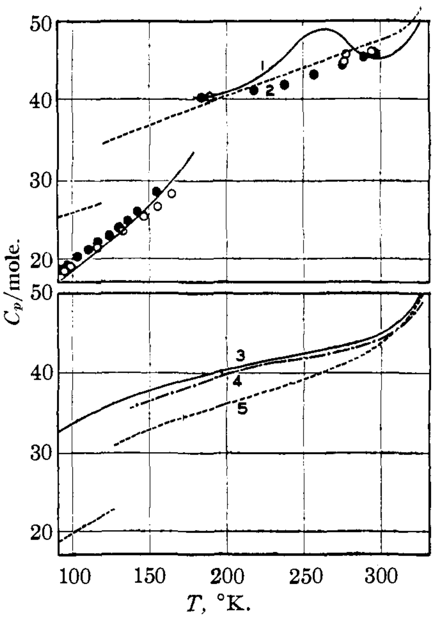

Fig. 5.—1, *n*-Hexane (●, Parks, Huffman, et. al. 1930; ○, Parks, Huffman, et. al. 1931); 2, 2-methylpentane; 3, 3-methylpentane; 4, 2,3-dimethylbutane; 5, 2,2-dimethylbutane.

The 2,2-dimethylbutane showed a very sharp transition point at 127.11°K. with a heat of transition of 1095 cal./mole. There was a rise of 9 cal. in the specific heat, and then melting occurred at 172.13°K. where the heat of fusion was 111 cal.$_{15}$/mole, and there was no change in the specific heat from the second solid form to the liquid state.

Entropy Data

With the experimental data of this work in conjunction with the third law of thermodynamics, the entropies at 298.1°K. of the substances studied have been calculated. The detailed entropy values are given in Table IV. In these calcula-

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(17) Johnston and Long, THIS JOURNAL, **56**, 31 (1934).
(18) Timmermans, *Bull. soc. chim. Belg.*, **44**, 17 (1935).
(19) Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930).
(20) Huffman, Parks, and Barmore, *ibid.*, **53**, 3876 (1931).
(21) Timmermans, *Bull. soc. chim. Belg.*, **43**, 626 (1934).
(22) Timmermans, *ibid.*, **36**, 502 (1927).
(22a) Smittenberg, Hoog and Henkes, THIS JOURNAL, accepted.

tions the extrapolation method of Kelley, Parks, and Huffman[23] was employed for estimating the entropy increases due to the crystals from 0 to 91°K. The various increments from 91 to 298.1°K. were obtained by the usual graphical methods from the experimental data. The results for the total entropy in cal.$_{15}$ per degree per mole are given as "$S°_{298}$ experimental" and are probably reliable to better than 3%.

TABLE IV

ENTROPIES OF THE COMPOUNDS IN E. U. per MOLE

	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I	*n*-Hexane
Crystals (0–91°)	10.17	10.52	13.35	12.70	13.07
Crystals (above 91°)	17.13	17.34	19.23	19.12	16.33
Fusion	10.75	10.02	10.48	9.62	16.57
Liquid (to 298.1°)	8.51	9.33	6.68	7.66	23.22
S°_{298} (experimental)	46.6	47.2	49.7	49.1	69.2
S°_{298} (predicted)	44.9	46.9	48.9	50.9	71.2

	2-Methylpentane	2,2-Dimethylbutane	CCl_4
Crystals (0–91°)	24.78	16.80	17.76
Crystals (to trans.)	7.79	7.45	18.86
Transition	...	8.61	4.87
Crystals (to m. p.)	...	9.96	2.97
Fusion	0.75	0.64	2.32
Liquid (to 298.1°)	36.59	20.94	5.65
S°_{298} (experimental)	69.9	64.4	52.4
S°_{298} (predicted)	66.7	62.2	60.7

It was also possible to predict the values for S°_{298} for these compounds from the results of previous studies and without access to the present data. Parks and Huffman[24] related the changes in molal entropy with various structural modifications in the organic molecule, and have assigned definite amounts of entropy for the introduction of particular atoms or groups. Using their empirical data the values for "S°_{298} predicted" have been computed. Comparing the S°_{298} values in Table IV shows that these predictions are in reasonable agreement with the experimental values except in the case of carbon tetrachloride. The case of carbon tetrachloride involved possibly other more complicated factors not considered in the calculations.

Free Energy Data

The free energies of formation for eight of these compounds were calculated by means of the fundamental relationship, $\Delta F = \Delta H - T\Delta S$.

The essential thermal data are given in Table V. In obtaining the values of ΔH_{298} the values 68,310 and 94,240 cal.[24] (pp. 44 and 46) have been used for the heats of combustion of hydrogen and graphitic carbon, respectively, in conjunction with the combustion value of the particular compound.

TABLE V

THERMAL DATA IN CALORIES$_{15}$ PER MOLE WITH ALL WEIGHTS REDUCED TO A VACUUM BASIS

Substance	ΔH^0_{298} (cal.$_{15}$)	ΔS^0_{298} (e. u.)	ΔF^0_{298} (cal.$_{15}$)
Carbon tetrachloride	−33,100	− 57.3	−16,000
Fluorobenzene	+ 9,585	− 73.8	+31,600
Chlorobenzene	+26,685	− 65.3	+46,200
Bromobenzene	+10,485	− 52.4	+26,100
Iodobenzene	+34,485	− 50.1	+49,400
n-Hexane	−49,010	−155.2	− 2,700
2-Methylpentane	−49,010	−156.5	− 2,400
2,2-Dimethylbutane	−49,010	−162.0	− 700

The following values for the heats of combustion were employed: for fluorobenzene Swietoslawski and Bobinska,[25] 745.8 kcal./mole; for chlorobenzene Redgrove,[26] 762.9 kcal./mole; for bromobenzene Kablukov and Perelman,[27] 746.7 kcal./mole; for iodobenzene Berthelot,[28] 770.7 kcal./mole. Because of the unreliability of the combustion data for carbon tetrachloride, the heat of fusion value of the liquid at 25°, $\Delta H_{298} = -33.1$ kcal./mole, was taken from the data of Parks and Huffman[24] (p. 197).

Kharasch[29] in his exhaustive study of the heat of combustion of organic compounds cites as an example the heats of combustion data for the isomeric heptanes which have been very carefully measured at the Bureau of Standards. All had the same heat of combustion, namely, 1416.2 kcal.$_{15}$/mole (within 2 kcal.). The heats of combustion for the isomeric pentanes are *also* all within the same limits with 833.6 kcal.$_{15}$/mole as the more probable value. On the basis of this argument it was assumed that the heats of combustion for the isomeric hexanes had the value 994.6 kcal.$_{15}$/mole (within the above limits). This value was obtained from the work done by Jessup[30] on *n*-hexane.

The tabulated ΔS°_{298} values represent the difference between the S°_{298} for each compound and the corresponding values for the entropies of the elements contained therein, which were calculated from the following atomic entropies[24] (pp. 44 and

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[23] Kelley, Parks, and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

[24] Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., N. Y., 1932, p. 209.

[25] Swietoslawski and Bobinska, *J. chim. phys.*, **24**, 545 (1927).

[26] Redgrove, *Chem. News*, **98**, 80 (1904).

[27] Kablukov and Perelman, *Compt. rend. Acad. Sci.* (U. S. S. R.), **1930A**, 519 (1930).

[28] Berthelot, *Ann. chim. phys.*, [7] **21**, 296 (1900).

[29] Kharasch, *Bur. Standards J. Research*, **2**, 373 (1929).

[30] Jessup, *ibid.*, **18**, 123 (1937).

46): C (graph), 1.3 e. u.; 0.5 H_2, 15.615 e. u.; 0.5 Cl_2, 26.62 e. u.; 0.5 Br_2, 16.3 e. u.; 0.5 I_2, 13.3 e. u.; and 0.5 F_2, 34.48 e. u.[31]

The molal free energies of formation of these compounds from their elements appear in the last column of the table. For the most part the accuracy of these values was limited by the accuracy of the combustion data employed, so that they were valid to about 3 or 4%.

The author wishes to express his appreciation to Dr. F. D. Rossini for making available the isomeric hexanes used in the work.

Summary

The construction and operation of a calorimeter suitable for determining specific heats together with heats of transition and fusion of organic compounds over the temperature range 100 to 320°K. has been described. The apparatus possesses the advantage of not employing a vacuum, and requiring only a 5- or 6-ml. sample.

The following compounds have been measured by this method: toluene, carbon tetrachloride, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, and the five isomeric hexanes. Two anomalies were brought to light. The specific heat of *n*-hexane showed a "hump" in the liquid state. The solid state of 2,2-dimethylbutane showed a large heat of transition some 50° below its melting point.

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[31] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., N. Y., 1923, p. 464.

The Fugacities in Gas Mixtures

BY I. R. KRICHEVSKY

Much time will be required before the slowly accumulating data on the $P-V-T$ relation of gas mixtures of different composition will permit computing the fugacity of the components of a gas mixture in accordance with the thermodynamic equation[1]

$$RT \ln f_i = RT \ln P + RT \ln N_i + \int_0^l \left(\overline{V}_i - \frac{RT}{P}\right) \mathrm{d}P \quad (1)$$

In this equation (1) f_i—is the fugacity of the component of the gas mixture, p—the total pressure, N_i—the mole fraction of the component in the mixture and $\overline{V}_i$—the partial molal volume of the component.

When solving thermodynamical problems dealing with high pressure, we shall still have to use for a long time approximate methods in computing the fugacity in gas mixtures.

The best of all known approximative methods is certainly the combination of constants in some proved equation of state; for instance those of Beattie–Bridgeman, Beattie[2] and Gillespie[3] have acquired in this field considerable success, and it is improbable that any other approximate method could compete for accuracy with this one.

Among other methods the approximate method of calculation of the fugacity in gas mixtures, known as the Lewis–Randall rule,[4] has been adopted widely. This rule is quite simple and is based, as Gillespie[5] has shown, on the law established by Amagat[6] with regard to the additive property of volumes. Representing an exact equation in the case of a component whose mole fraction is insignificantly or, to be more exact, infinitesimally differing from a unit, the rule of Lewis–Randall did not withstand experimental check,[7,8] when applied to other concentrations.

Randall and Sosnick[9] in a very important paper have pointed out the limitations of the Lewis and Randall rule. "This latter rule has been shown to hold as an approximation and as a limiting law for gaseous solutions above the critical temperature of the gases, and for a limited range of total pressure for the solute gas below its critical temperature."[9]

Apart from the Amagat law, other "laws" are known for the determination of the $P-V-T$ relation in gas mixtures, such relations being known for pure gases. For the determination of the

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[1] Gillespie, THIS JOURNAL, **48**, 28 (1926).

[2] Beattie, *ibid.*, **51**, 19 (1929); Beattie and Ykehara, *Proc. Am. Acad. Arts Sci.*, **64**, 127 (1930).

[3] Gillespie, *Phys. Rev.*, **34**, 352 (1929).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

[5] Gillespie, *Phys. Rev.*, **34**, 352, 1605 (1929).

[6] Amagat, *Ann. chim. phys.*, [5] **19**, 384 (1880); *Compt. rend.*, **127**, 88 (1898).

[7] Merz and Whittaker, THIS JOURNAL, **50**, 1522 (1928).

[8] Gibson and Sosnick, *ibid.*, **49**, 2172 (1927).

[9] Randall and Sosnick, *ibid.*, **50**, 967 (1928).