

Construction of an adiabatic calorimeter.^a Thermodynamic properties of standard *n*-heptane from 155 to 270 K and of 2,2-dichloropropane from 135 to 270 K

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The construction of an adiabatic calorimeter is described. Measurements have been made of the heat capacity of a standard sample of *n*-heptane and of 2,2-dichloropropane. The estimated errors are generally within 0.5 per cent.

1. Introduction

Several adiabatic calorimeters have been described in the literature.⁽¹⁾ The calorimeter described in this paper was built with the intention to use it for measuring heat capacities of binary systems of organic compounds. Measurements can be made by one operator and continuous heating or cooling curves are readily obtained. The performance of the apparatus was checked with a standard sample of *n*-heptane.

2,2-Dichloropropane is of interest as a globular molecule belonging to the series $C(CH_3)_xCl_{4-x}$, where x varies from zero to four. For this series enthalpies of mixing are available⁽²⁾ and two binary systems have been investigated by calorimetric methods.^(3, 4) Several other investigations such as measurements of dielectric constants, X-ray diffraction work, and sound velocity measurements have been carried out.

The measurement of the enthalpies of transition and of fusion of 2,2-dichloropropane, given in the second part of this paper, completes these values for this series.^(5, 6)

2. Apparatus

THE CRYOSTAT

The adiabatic-type calorimeter has been previously described in detail in the thesis of the author. A short description is given here. The general design is shown in figure 1. Cooling of the calorimeter was generally obtained by immersing the vacuum

^a Based upon a dissertation entitled *Construction of an adiabatic calorimeter and measurement of the system carbon tetrachloride + cyclohexanone*. Copies available upon request to the author.

can (1) in liquid nitrogen. For measurements above room temperature, water was circulated through the dewar (2). The sample container (3) was surrounded by two shields (4, 5). The inner shield consisted of a frame (6) and a cylinder with a base.

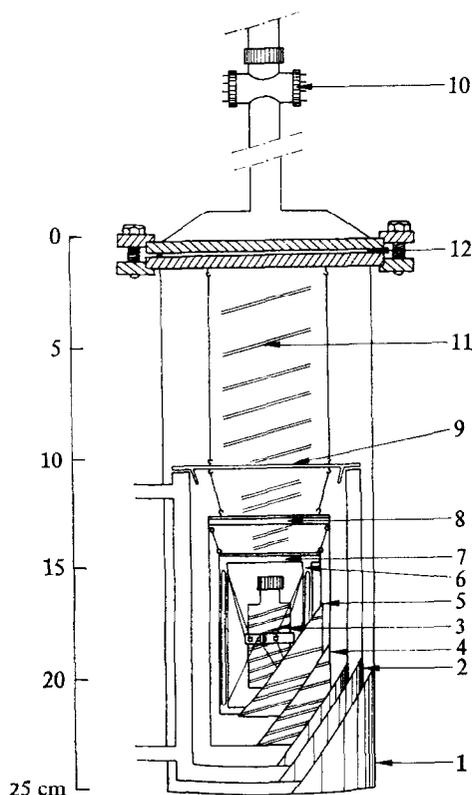


FIGURE 1. Cross section of the cryostat; (1), vacuum can; (2), dewar; (3), sample container; (4), outer shield; (5), inner shield; (6), frame of the inner shield; (7, 8), covers of the shields; (9), lid of the dewar; (10), lead through connector; (11), wire bundles; (12), O-ring closure.

The sample container was clamped in a ring which was kept in place by the thermopile which detected temperature differences between the ring and the frame. The junctions of the thermopile were soldered on small pieces of copper-teflon-copper sheath. We used a pile of six thermocouples, made of chromel and constantan wires, 0.1 mm diameter.

The wires coming from the sample container were divided into measuring and current leads. The two wire bundles were fitted with Apiezon T in spiral grooves impressed in the covers of both shields (7, 8). After passing through a plate (9) covering the dewar, they were brought out by means of two multipin lead-through connectors (10). The shields were made of nickel-plated copper (0.35 mm); thermocoax heating wire (Philips code no. 156.810) was soldered non-inductively on the cylindrical parts; the spacings between the heating wires were made smaller near the top and the bottom.

Between the inner and the outer shield a pile of six thermocouples measured the temperature difference. The junctions were not soldered to the shields but kept in place by two teflon rings.

Vacuum was obtained by two mercury diffusion pumps, backed by an Edwards rotary pump; measurements were made at pressures of 10^{-5} Torr or less.†

THE SAMPLE CONTAINER

The sample container was made of pure 0.4 mm silver. At the base a thermometer well was constructed, the 100 Ω platinum resistance thermometer was melted in with indium.

For the heater thermocoax wire 0.5 mm diameter was used, the resistance being about 22 Ω . It was soldered in two spirals cut in the jacket. The middle section of the jacket was thicker: thus after cutting in the spirals and soldering the heating wire, this section served as a smooth surface for the clamping ring.

Closure was effected by means of a screw cap which pressed a teflon sheath into the sharp stainless steel edge of the container neck. These teflon sheaths could be re-used several times, the closure was leak-proof under all the circumstances.

The total mass of the sample container was 16 g, the heat capacity at room temperature about 5.6 J K⁻¹, and the volume 9 cm³.

MEASUREMENT OF THE TEMPERATURE

A three-point Wheatstone bridge method was used in order to measure the resistance of the 100 Ω platinum thermometer. A Bleeker decade resistance was used as the variable part of the bridge. The lowest decade consisted of 0.01 Ω steps. The bridge signal was registered on a 20 μ V Kipp Micrograph (type BD 5). An unbalance of 0.01 Ω , at a measuring current of 1 mA, resulted in a deflexion of about 60 mm. The sensitivity of the method was excellent: 2×10^{-4} Ω could be resolved. A disadvantage was the difficulty encountered in calibrating the thermometer.

We calibrated the thermometer on the known melting temperatures of carbon tetrachloride and *n*-heptane and the transition temperature of carbon tetrachloride. The absolute accuracy of this calibration was fairly low; we estimated it to be about 0.05 to 0.1 K. Temperature differences on the other hand, which were needed for the determination of heat capacities could be measured with ease and accuracy.

MEASUREMENT OF THE ENERGY INPUT

The energy input circuit consisted of a 12 V d.c. power supply, two variable resistances, a 10 Ω standard resistance, and the heating wire of the sample container. The potential drop over the heater and over the 10 Ω standard resistance were measured with a six-digit digital voltmeter. When no heat input was made, a 300 Ω resistance was switched in.

The duration of the energy input was measured with an electric chronometer which started and stopped through a sudden potential change over one of the variable resistances.

† Torr = (101.325/760) kPa.

THE REGULATION OF THE SHIELDS

The circuits for the inner and the outer shield were essentially alike. The potential of the thermopile was fed to a Honeywell-Brown servoamplifier (part no. 35170-35). The servo-motor started to rotate at a signal of $0.5 \mu\text{V}$. The servo-motor rotated a ten-turn potentiometer which was in series with the shield heater; the motor also operated a microswitch with which a variable resistance could be short-circuited. A slip-coupling was used to protect the potentiometer. The advantage of this regulation was its symmetry. With the microswitch an on-off regulation of part of the current was obtained; when the on-period was longer than the off-period, the servo-motor lowered the series resistance in the circuit and vice versa. If the proper choice of resistances is made, the regulation will be symmetrical after a few periods.

The sample heating circuit was closed by a three-fold switch. When this circuit was closed, additional current was required for the shields, which have to follow the sample container. This was obtained by short-circuiting a variable resistance in the shield circuits with the same switch.

A "set-off" circuit, with which the control point of the regulation could be changed, was built in. The outer shield was maintained with the "set-off" about 1 K below the inner one. The obtained regulation of the inner shield was sinusoidal with an amplitude of about $0.5 \mu\text{V}$ when no energy was supplied to the sample and about $2 \mu\text{V}$ during the input periods.

STANDARDIZATION OF THE APPARATUS

The standard resistances used were compared with a standard resistance of the Fysisch Laboratorium, Rijksuniversiteit Utrecht; the error was assumed to be smaller than 0.01 per cent. The chronometer was checked against standard radio time signals; the error in the time measurement was usually less than 0.01 per cent. A correction for the heat developed in the leads between the sample container and the inner shield was estimated.

3. Measurements on a standard sample of *n*-heptane

In order to verify the performance of the apparatus, the heat capacity and the enthalpy of fusion of *n*-heptane, obtained from the National Bureau of Standards in Washington, was measured. Extensive measurements of this sample have been reported by the Bureau and compared with the results of other workers in this field.⁽⁷⁾ The purity of the sample was determined in the calorimeter from temperature measurements at different stages of melting. The purity calculated is 99.968 moles per cent; this is not as high as reported by the Bureau: 99.999 moles per cent. The transfer in air of the sample may be the cause of a contamination.

HEAT CAPACITIES

We made high- and low-filling experiments under identical conditions. The samples used had a mass of 4.7873 and 0.7555 g, respectively. The individual measurements and the values for the empty container are given in the tables 1, 2, and 3. The tables

TABLE 1. Measured heat capacity of the sample and the sample container. High-filling experiment: 4.7873 g

$\frac{\langle T \rangle}{\text{K}}$	$\frac{\langle C_p \rangle}{\text{J K}^{-1}}$	$\frac{\Delta T}{\text{K}}$	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\langle C_p \rangle}{\text{J K}^{-1}}$	$\frac{\Delta T}{\text{K}}$
	run 1		176.7611	11.851	3.6623
192.8184	14.780	0.7196	179.5808	12.003	1.9761
193.4161	14.715	0.4755	185.1059	14.753	2.9707
193.9004	14.796	0.4930	187.8262	14.761	2.4691
194.3662	14.823	0.4358	194.6046	14.800	2.7305
			197.4656	14.817	2.9821
	run 2		200.7007	14.838	3.4737
166.1626	11.173	0.8180	205.0560	14.882	5.2192
167.8059	11.332	2.4663	210.1610	14.836	4.9992
172.0032	11.499	5.9424	213.9166	14.922	2.5005
175.3457	11.687	0.7462	215.6641	14.924	0.9994
176.2265	11.813	0.9898			
177.3384	11.847	1.2341		run 6	
178.4484	12.009	0.9865	160.4493	11.041	9.8254
179.5054	12.000	1.1316	170.4489	11.505	10.1728
180.6883	12.219	1.2350	185.9203	14.790	1.7021
181.6259	12.916	0.6430	187.9895	14.795	2.4304
			190.5735	14.797	2.7297
	run 3		193.0544	14.814	2.2245
130.7311	9.799	2.4286	195.4100	14.819	2.4743
152.0874	10.694	1.7260	197.8913	14.825	2.4801
177.4811	11.829	1.4906	200.2998	14.845	3.4794
	run 4			run 7	
235.6227	15.192	5.0334	157.4361	10.906	3.7063
240.6678	15.288	5.0528	161.7676	11.095	4.4285
247.0057	15.383	7.6060	167.6499	11.361	7.3474
252.0725	15.448	2.5075	173.6327	11.688	5.1629
			188.0207	14.807	2.4035
	run 5		191.0741	14.815	3.6451
161.4235	10.964	7.3497	194.6213	14.834	3.4369
167.5566	11.345	4.9137	197.5699	14.827	2.4514
170.0146	11.015	4.9110	200.9106	14.837	4.2259

TABLE 2. Measured heat capacity of the sample and the sample container. Low-filling experiment: 0.7555 g

$\frac{\langle T \rangle}{\text{K}}$	$\frac{\langle C_p \rangle}{\text{JK}^{-1}}$	$\frac{\Delta T}{\text{K}}$	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\langle C_p \rangle}{\text{JK}^{-1}}$	$\frac{\Delta T}{\text{K}}$
	run 1			run 3	
163.1890	5.877	7.3797	153.5781	5.727	4.4342
169.3397	5.973	4.9209	162.2827	5.873	12.9844
175.0152	6.061	6.4332	173.7830	6.051	10.4780
179.4159	6.159	2.3653	187.6609	6.696	2.8125
187.7718	6.610	2.4970	191.7417	6.659	5.3486
191.5252	6.651	4.9524	196.7764	6.688	4.7205
195.7761	6.661	3.4943			
200.5052	6.700	6.4772			
206.4994	6.736	4.9894			
	run 2		165.6735	5.913	3.7265
232.9115	6.902	3.9402	173.7766	6.044	4.0659
236.5263	6.917	3.2868	177.6956	6.101	3.7925
239.5601	6.936	2.7779	188.3594	6.631	3.8326
245.5238	6.969	9.1330	192.0646	6.660	3.5801
254.5607	7.018	8.9317	196.1942	6.680	4.6792
262.9901	7.041	7.9472			
				run 4	

TABLE 3. Measured heat capacity of the empty sample container

$\frac{\langle T \rangle}{\text{K}}$	$\frac{\langle C_p \rangle}{\text{JK}^{-1}}$	$\frac{\Delta T}{\text{K}}$	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\langle C_p \rangle}{\text{JK}^{-1}}$	$\frac{\Delta T}{\text{K}}$
	run 1			run 2	
141.6384	4.649	13.1107	255.6360	5.465	12.8598
154.6057	4.802	12.8070	267.9466	5.511	11.7632
169.4827	4.949	16.9405	279.7484	5.527	11.8450
186.9738	5.089	18.0539	291.6105	5.627	11.8957
205.3485	5.095	19.0724			
221.3460	5.293	13.2564		run 3	
233.9233	5.357	11.7819	234.1412	5.358	10.1151
244.3070	5.389	8.9777	247.6733	5.403	16.9788
			262.2812	5.459	12.2286
			276.8585	5.514	16.9475
			286.8874	5.555	3.0966

contain the mean temperature $\langle T \rangle$ of the measured interval, the mean heat capacity $\langle C_p \rangle$ of the sample + container or container and the temperature interval ΔT .

SMOOTHED HEAT CAPACITY VALUES

The smoothed heat capacities given in table 4 were calculated in two ways. First $C_p(1)$ from the high-filling and the low-filling experiments, secondly $C_p(2)$ from the high-filling experiments minus the values obtained by smoothing the values for the empty container. Both sets of values were compared with the smoothed values of the N.B.S. $C_p(3)$, and the deviations of our values are also given in table 4.

TABLE 4. Smoothed values of the heat capacity of *n*-heptane and comparison with the values of the N.B.S.

T K	$C_p(1)$ J K ⁻¹ mol ⁻¹	$C_p(2)$ J K ⁻¹ mol ⁻¹	$C_p(3)$ J K ⁻¹ mol ⁻¹	$\frac{100\{C_p(1)-C_p(3)\}}{C_p(3)}$	$\frac{100\{C_p(2)-C_p(3)\}}{C_p(3)}$
solid:					
155	125.6	125.7	125.8	-0.1	-0.0
160	128.3	128.6	129.0	-0.6	-0.5
165	131.0	131.5	132.5	-1.1	-0.7
170	135.7	136.0	136.0	-0.3	0.0
175	139.8	140.4	139.8	0.0	0.4
180	145.6	145.9	145.1	0.3	0.5
182.56 ^a	148.8	148.6	148.6	0.1	0.0
liquid					
182.56 ^a	203.2	203.0	203.1	0.0	-0.0
185	201.5	201.8	202.6	-0.1	-0.4
190	202.5	202.5	201.9	0.3	0.3
195	202.5	202.6	201.5	0.5	0.6
200	202.3	202.3	201.3	0.5	0.5
205	202.5	202.4	201.4	0.5	0.5
210	202.5	202.2	201.7	0.4	0.3
215	—	201.9	202.1	—	-0.1
220	—	202.7	202.7	—	-0.0
225	—	203.9	203.5	—	0.2
230	—	204.9	204.4	—	0.3
235	206.1	205.7	205.4	0.3	0.2
240	206.1	206.1	206.5	-0.2	-0.2
245	208.4	208.3	207.6	0.4	0.3
250	209.8	209.5	208.9	0.4	0.3

^a Extrapolated.

ENTHALPY OF FUSION

Each filling was measured three times. The results are given in table 5. The table contains the temperature interval T_1 to T_2 , the total energy input q , the correction for the heat capacity of the sample and the sample container $C_p(\text{corr})$, a drift correction D , and the calculated enthalpy of fusion ΔH . No correction was applied for premelting as the effect was too minute to be of any importance. The values found are slightly higher than those reported by the N.B.S.; this may be attributed to the

handling of the sample in air. The mean value of the high-filling experiments is $14054.0 \text{ J mol}^{-1}$, of the low-filling experiments $14068.0 \text{ J mol}^{-1}$. The mean value reported by Douglas and others⁽⁷⁾ from the N.B.S. is $14022.5 \text{ J mol}^{-1}$, with a standard deviation of 9.4 J mol^{-1} .

TABLE 5. Enthalpy of fusion of standard *n*-heptane

$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{q}{\text{J}}$	$\frac{C_p(\text{corr})}{\text{J}}$	$\frac{D}{\text{J}}$	$\frac{\Delta H}{\text{J mol}^{-1}}$
181.3044	192.4542	833.015	161.70	—	14050.9
175.5410	185.0659	792.720	121.05	0.07	14056.8
176.4824	186.8401	807.750	136.27	—	14054.3
180.6975	186.5475	144.33	38.57	—	14026.7
179.5906	186.4446	150.09	43.86	—	14088.7
179.2854	189.0679	169.41	63.18	—	14088.7

4. 2,2-Dichloropropane

MATERIAL

We employed 10 cm^3 samples obtained from Fluka. These samples were distilled once to remove the added stabilizer. The mass of the sample was 3.6550 g. First the melting curve was determined by several energy inputs. The reciprocal of the fraction

TABLE 6. Experimental heat capacity of 2,2-dichloropropane

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{ mol}^{-1}}$
	run 1		run 4
171.52	102.43	196.01	129.60
174.74	105.34	204.82	131.96
177.85	107.60		
180.97	111.33		run 5
192.53	128.44	197.05	129.58
195.64	129.37	200.71	130.10
199.12	130.68	207.98	132.38
		217.22	134.44
	run 2		run 6
207.84	132.08	137.65	84.11
214.03	133.55	152.54	91.76
220.11	135.44	168.59	100.89
240.54	148.59	178.66	109.09
	run 3		run 7
203.71	131.21	192.04	130.20
212.33	133.80	197.57	130.49
220.94	136.02	208.27	133.12
244.95	148.84	220.10	135.93
253.04	149.58	245.18	149.43
260.25	150.24	252.09	149.77
266.66	150.80	258.86	150.67

melted was plotted against the equilibrium temperature. From these results the melting temperature of the pure sample was determined to be 239.25 K and the purity 99.72 moles per cent. Timmermans⁽⁶⁾ reported the melting temperature to be 239.36 K and Stull, Westrum, and Sink⁽⁵⁾ 239.4 K.

HEAT CAPACITIES

The values measured and the values for the smoothed curve are given in the tables 6 and 7.

TABLE 7. Smoothed heat capacity curve of 2,2-dichloropropane at rounded temperatures

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$
solid I:		200	130.5
140	85.2	210	133.0
150	90.4	220	135.5
160	95.6	230	137.9
170	101.7	239.25	140.2
180	110.0		
188	117.6	liquid:	
solid II:		239.25	148.5
188	127.6	250	149.5
190	128.0	260	150.5
		270	151.4

ENTHALPIES OF TRANSITION AND OF FUSION

Both quantities were measured three times. The results are given in table 8. A very small pre-effect was observed in the transition. The maximum of this effect was estimated to occur at 184.8 K. This effect could not be measured separately, the corresponding heat effect being estimated to be 100 J mol⁻¹. This effect might have to be attributed to the impurity of the sample. However, other compounds in this

TABLE 8. Enthalpy of transition ΔH_{tr} and enthalpy of fusion ΔH_m of 2,2-dichloropropane

	$\frac{\Delta H_{tr}}{\text{J mol}^{-1}}$		$\frac{\Delta H_m}{\text{J mol}^{-1}}$
run 1	5985 ^a	run 3	2340
run 4	5954 ^a	run 5	2355
run 6	5997 ^a	run 7	2329
mean value:	(5979 ± 20)	mean value:	(2341 ± 14)

^a Including the pre-effect mentioned.

series: 1,1,1-trichloroethane⁽⁶⁾ and *t*-butylchloride⁽⁵⁾ also show a transition below the rotational transition. So it cannot be excluded that the effect measured belongs to the pure substance.

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