SUPERSONIC VELOCITY IN GASES AND VAPOURS.

PART V. SPECIFIC HEATS OF VAPOURS OF ACETONE, BENZENE, CYCLOHEXANE, *n*-HEXANE, METHYL, ETHYL, AND *n*-PROPYL ETHERS.

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INTRODUCTION.

In Parts I, II, III and IV (This Journal, 1938, *21A*, 245, 455, 477 and 1939, *22A*, 1), the author has given an account of the difficulties encountered in the measurement of supersonic velocity in gases and vapours. As a result of numerous preliminary experiments, it was found essential to work in narrow tubes. It was also found necessary to measure the frequencies accurately on the spot. In the present paper, the author has presented the results of measurements of the wave lengths in vapours of acetone, benzene, cyclohexane, *n*-hexane, methyl ether, ethyl ether and propyl ether, superheated to 97.1° and 134°, at 685 mm. pressure, and also the values of the specific heats calculated from the supersonic velocity. The results are compared with the values obtained from spectroscopic data.

EXPERIMENTAL.

The apparatus used was the same as described in Fig. 1, Part I. Water was used in the boiler for maintaining a constant temperature, 97.1° in the jacket, and meta-xylene, for 134°. As already mentioned, a slow stream of the vapour was maintained in the apparatus to avoid leaks at the gland packing for the piston rod. Acetone was purified by the sodium iodide method, and benzene, by crystallisation. Methyl ether was prepared by passing methyl alcohol vapour through sulphuric acid at 125°, and absorbing the gas in sulphuric acid. The gas was liberated by adding water and dried over barium oxide. *n*-Propyl ether was prepared from *n*-propyl alcohol by catalytic dehydration over alum. (cf. Gajendragad and Jatkar, Jour. Ind. Chem. Soc. 1935, **12**, 486). All the liquids were purified by fractionation.

The details of the wave length measurements are given in the following tables (1—11).

TABLE 1.

Acetone 97.1°

Frequency 49.42 Khz.

$\downarrow n\ \lambda/2$	Screw reading mm.	$\uparrow n\ \lambda/2$	Screw reading mm.	$\downarrow n\ \lambda/2$	Screw reading mm.	$\uparrow n\ \lambda/2$	Screw reading mm.
0	7.25	52	6.32	0	7.15	52	6.15
1	9.70	51	8.70	1	9.50	51	8.65
2	12.25	50	11.40	2	12.05	50	11.25
12	36.25	49	13.55	3	14.50	49	13.50
22	60.55	48	16.05	4	16.98	48	15.85
32	84.50	47	18.55	5	19.15	47	18.45
42	108.80	46	20.85	15	43.35	46	20.80
43	110.95	45	23.30	25	67.50	45	23.10
44	113.35	35	47.55	35	91.60	44	25.50
45	116.95	25	71.50	45	115.70	34	49.75
46	118.15	15	95.60	46	118.05	24	73.85
47	120.55	5	119.70	47	120.45	14	97.93
48	122.95	4	122.25	48	122.85	4	122.10
49	125.45	3	124.70	49	125.40	3	124.65
50	127.95	2	127.05	50	127.88	2	126.90
51	130.45	1	129.55	51	130.30	1	129.35
52	132.90	0	132.15	52	132.75	0	132.05
	$50\ \lambda/2$		$50\ \lambda/2$		$50\ \lambda/2$		$50\ \lambda/2$
50—2	120.70		120.75		120.73		120.80
51—1	120.75		120.85		120.80		120.70
52—2	120.65		120.73		120.70		120.75
	120.70		*120.78*		*120.73*		*120.75*
Mean $50\ \lambda/2$ = 120.74 mm. $\lambda/2$ = 2.4148 mm.				Mean $50\ \lambda/2$ = 120.74 mm. $\lambda/2$ = 2.4148 mm.			
Velocity $= n\lambda$ = **238.68 meters per sec.**				Velocity $= n\lambda$ = **238.68 meters per sec.**			

TABLE 2

Acetone 97.1°

Frequency 95.822 Khz.				Frequency 94.159 Khz.				126.648 Khz.	
$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm	$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.
0	5.70	102	5.15	0	5.90			0	5.28
1	6 88	101	6.40	1	7 15	101	6.47	1	6.15
2	8.25	100	7.75	2	8.48	100	7 85	2	6.85
3	9.50	99	9.00	3	9 78	99	9.18	15	19.45
4	10.70	98	10 22	4	11.10	98	10.31	17	20.90
14	23.30	97	11.45			97	11 70	18	21.85
24	35.65	96	12.80			96	13.05	22	26.00
34	48.05	95	14 10			95	14.28	24	27.90
44	60.55	94	15 33			94	15.43	44	46.75
54	72.98	93	16 58			84	28 12	67	68.15
64	85.30	83	28.85			64	53.45	78	78 40
74	97 83	73	41 28	44	61.68			88	87.88
84	110.20	63	53.80			44	78 93	98	97.35
94	122.75	53	66 10	64	87 05	24	104.25	108	106.88
95	123.90	43	78 75	84	112.23			118	116.18
96	125.15	33	91.00	94	124 98			132	129.30
97	126.38	23	103 55	97	128.80			133	130.20
98	127.73	13	115.95	98	129.95	4	129 50		
99	128.90	3	128 48	99	131 23	3	130 75		
100	130.12	2	129.78	100	132 49	2	132.10		
101	131.33	1	130.80	101	133.83	1	133 36		
102	132.70	0	132.30	102	135 05	0	134.67		
	$100\ \lambda/2$		$100\ \lambda/2$		$100\ \lambda/2$		$100\ \lambda/2$		$132\ \lambda/2$
100—0	124.42		124.55		126.59	100—0	126 82	132—0	124.02
101—1	124,45		124 40		126 68	101—1	126 89	133—1	124.05
102—2	124.45		124.63		126.57				
	124.44		*124.53*		*126.61*		*126.85*		*124.035*
Mean $100\ \lambda/2$ = 124 48 mm. $\lambda/2$ = 1.2448 mm.				Mean $100\ \lambda/2$ = 126.73 mm. $\lambda/2$ = 1.2673 mm.				$\lambda/2$ = 0.9396 mm.	
Velocity = $n\lambda$ = **238.56 meters per sec.**				Velocity = $n\lambda$ = **238 6 meters per sec.**				Velocity = $n\lambda$ = **238.0 m./sec.**	

The method used to measure the wave length was, to record the screw readings corresponding to the positions of the reflector for a few consecutive peaks, as the reflector was advanced towards the crystal oscillator, after which, readings were taken at intervals of 10 $\lambda/2$. Finally, measurements were again taken for consecutive peaks. The middle sets of readings helped to check the

TABLE 3

Acetone 134°

Frequency 93.887 Khz.				Frequency 126.283 Khz.			
$n\lambda/2$	Screw reading mm	$n\lambda/2$	Screw reading mm.	$n\lambda/2$	Screw reading mm.	$n\lambda/2$	Screw reading mm.
0	6.44	97	4.38	0	7.50		
		96	5 77				
1	7.65	95	7.15	1	8.35	126	8.95
2	8.94	94	8.47			125	10.05
3	10.39	93	9.82			124	10.90
4	11.65	83	23.05			123	12.00
14	24.88	73	36 42	6	13.38	122	13.00
24	38.33	63	49.82	16	23.38	112	22.85
34	51.75	53	63.24	27	33 68	102	33.00
44	65.08	43	76.58	38	44.30	92	42.70
54	78.50	33	90.15	48	54.26	82	52.77
64	91.98	23	103.45	59	65.24	72	62.65
74	105.27	13	116 62	69	75.08	62	72.58
84	118 53	3	130 08	79	85.35	52	82.56
94	132.00	2	131.50	90	96 10	42	92.55
95	133.35	1	132.77	100	106.00	32	102.45
96	134.65	0	134.13	110	115.85	22	112.62
	94 $\lambda/2$		94 $\lambda/2$	120	125.88	12	122.28
94—0	125.56	94—0	125 66	126	131.78	2	132.40
95—1	125.70	95—1	125.62	127	132.88	1	133.28
96—2	125 71	97—3	125.70	128	133.70	0	134.28
				129	134.70		
				130	135.70		
					129 $\lambda/2$		124 $\lambda/2$
				129—0	127.20	124—0	123.38
				130—1	127.35	125—1	123.23
						126—2	123.45
	125 69		*125.66*		*127 27*		*123.35*
Mean 94 $\lambda/2$ = 125.68 mm $\lambda/2$ = 1.3370 mm.				$\lambda/2$ = 0.9948 mm.			
Velocity = $n\lambda$ = **251.05 meters per sec.**				Velocity = $n\lambda$ = ***251.15 meters per sec.***			

total number of half wave lengths measured, and the average for successive intervals for, say, 50 to 100 wave lengths, was found out by making use of the first and the last set of readings in each table, In the same manner, sets of readings were taken when the reflector was moved away from the crystal oscillator. The mean of these two sets of readings was utilized in measuring the velocity. It was found

TABLE 4(*a*)

Benzene 97.1°

Frequency 94.16 Khz.		Frequency 127 Khz.	
$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.
0	133.70	0	134.67
1	132 64	1	133.93
2	131 56	2	133.13
3	130.47	3	132 30
4	129.39	4	131.53
24	108.05	5	130.72
44	86.56	15	122.75
64	65.15	25	114 77
84	43.68	35	106 90
104	22 20	45	98 92
114	11.48	55	90.88
115	10 45	75	75.00
116	9.35	85	67.05
117	8 30	95	59.08
118	7 18	105	51 10
119	6.12	115	43.20
		116	42 38
		117	41.45
		118	40 82
	115 $\lambda/2$		115 $\lambda/2$
0—115	123.25	0—115	91.47
1—116	123.29	1—116	91.55
2—117	123.26	2—117	91.58
3—118	123.29	3—118	91.48
4—119	123 27		
	123 27		*91.475*
Mean 115 $\lambda/2$ = 123.27mm. $\lambda/2$ = 1.0719mm		Mean 115 $\lambda/2$ = 91.475mm $\lambda/2$ = 0.7954mm.	
Velocity = nλ = **201.9 meters per sec.**		Velocity = nλ = **202.05 meters per sec.**	

ıt the wave lengths were systematically 1 part in a 1,000 smaller ıen the piston was moved towards the crystal than when it was ›ved away from the crystal. This was obviously due to the temrature coefficient of expansion of the pyrex glass reflector. The actual ve length was correctly represented by the mean of the two sets readings, when the reflector was moved in and when it was moved t respectively.

TABLE 4 *(b)*

Benzene 97.1°

Frequency 49.42 Khz.				Frequency 95.82 Khz.	
$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.
0	2.00	1	1.90	0	133.92
1	4 00	2	4.00	1	132.88
2	6.10	3	5 95	2	131.79
3	8 35	4	7.95	3	130 73
4	10.25	5	10.00	4	129.65
5	12 40	6	12.05	24	108.68
6	14 35	7	14.05	44	87.60
7	16.20	8	16.00	64	66.45
8	18 30	9	18 80	84	45 38
10	22.50	10	20 08	104	24.30
12	26 65	11	22.20	118	9.50
13	29 00	12	24.24	120	7 50
15	32 90	13	26.30	121	6.43
16	35 25	23	46 65	122	5.40
17	37.00	33	67.50		
18	39.45	43	87.85		
19	41 70	53	108.10		
21	45 20	54	110.25		
31	65.50	55	112.35		
41	85.65	56	114.42		
51	106 15	57	116 48		
52	108 40	58	118.53		
53	110 48	59	120 60		
	50 $\lambda/2$		55 $\lambda/2$		120 $\lambda/2$
51−1	102 15	56−1	112 32	0−120	126.42
52−2	102.30	57−2	112 48	0−121	126.45
53−3	102.13	58−3	112.58		
		59−4	112 65		
		60−5	112 73		
		61−6	112.73		
	102.20		*112.58*		*126.44*
50 $\lambda/2$=102 20 mm. Mean $\lambda/2$=2 044 mm		55 $\lambda/2$=112 58 mm. Mean $\lambda/2$=2.047 mm.		120 $\lambda/2$=126.44 mm. Mean $\lambda/2$=1.054 mm.	
Mean $\lambda/2$=2 0455 mm **Velocity = $n\lambda$ =202.18 meters per sec.**				Mean $\lambda/2$=1 054 mm **Velocity= $n\lambda$ =202.0 meters per sec.**	

The crystal oscillators used were those used in Part IV, where the details of the measurements of their absolute frequencies are given.

Tables 1 and 2 show the results for the measurement of velocity in acetone vapour at 97.1°. Table 3 shows the readings at 134° in the same vapour. These results show that there is no dispersion of

Table 5

Benzene 134°

Frequency 93.825 Khz.				Frequency 127 Khz.	
$n\lambda/2$	Screw reading mm.	$n\lambda/2$	Screw reading mm.	$n\lambda/2$	Screw reading mm.
0	108.00	0	7 62	0	131.40
1	106.87	1	8.77	1	130 58
2	105.70	2	9 85	2	129.74
3	104.57	3	10.98	3	128.92
4	103.48	4	12 14	4	128.12
14	92.22	14	23.55	5	127.20
24	80.80	24	34.86	15	118 68
34	69.55	34	46 27	40	97.75
44	58 10	44	57.48	50	89 33
54	46 83	54	68 93	60	80.88
64	35 45	64	80.22	70	72 43
74	24.20	74	91.60	80	64.00
84	12.76	84	102.80	90	55.55
85	11.58	94	114.20	100	47.35
86	10.48	104	125 40	115	34 45
87	9.38	105	126 58	126	25.40
88	8 30	106	127.68	133	19.34
89	7 20	107	128.80	134	18.50
90	6 05	108	129 98		
		109	131.12		
		110	132 23		
	$86\lambda/2$		$105\lambda/2$		$133\lambda/2$
0—86	97.52	105—0	118 96	0—133	112.06
1—87	97.44	106—1	118 91	1—134	112 08
2—88	97.40	107—2	118.95		
3—89	97.37	108—3	119.00		
4—90	97.43	109—4	118.98		
	97·44		*118.96*		*112·07*
$86\lambda/2$ = 97.44 mm. $\lambda/2$ = 1.133 mm		$105\lambda/2$ = 118.96 mm $\lambda/2$ = 1.133 mm.		$133\lambda/2$ = 112.07 mm $\lambda/2$ = 0 8426 mm.	
Velocity = $n\lambda$ = **212.60 meters per sec.**				Velocity = $n\lambda$ = **212.71 meters per sec.**	

velocity from 49 Khz. to 126 Khz., the mean value for the velocity being 238.4 ± 0.1 m./sec. at 97.1°. The velocity increases to 251.1 ± 0.05 m./sec. at 134°.

Tables 4 and 5 show the details of the wave length measurements in benzene vapour at different frequencies at 97.1° and 134° respectively. There is no dispersion of velocity in the present

TABLE 6.

Ethyl Ether 97.1°

Frequency 49.42 Khz				Frequency 127 Khz			
$\downarrow n\ \lambda/2$	Screw reading mm.	$\uparrow n\ \lambda/2$	Screw reading mm.	$\downarrow n\ \lambda/2$	Screw reading mm.	$\uparrow n\ \lambda/2$	Screw reading mm
0	7 90	59	7.10	0	6.10	150	4 85
1	10.15	58	9.30	1	6 85	149	5.68
2	12.30	57	11 43	2	7.70	148	6.50
13	35 05	53	20 85	3	8.48	147	7.25
22	55.85	43	40 73	4	9.28	146	8 10
33	77.00	33	61,48	5	10.24	145	8.85
44	100.00	23	82.32	6	10.96	144	9.73
54	120.75	13	103 20	7	11.74	124	26 05
56	124.85	3	124.16	8	12 60	103	43.22
57	127.20	2	126 43	29	29.73	80	62.03
		1	128 50	49	46 18	58	80.00
		0	130 55	72	64.82	36	97 80
	55 $\lambda/2$		57 $\lambda/2$	95	83 42	15	114.87
56 — 1	114.70		119.12	115	99 80	5	122 96
57 — 2	114.90		119 20	136	118.85	4	123.82
			119,23	157	133 98	3	124.62
				158	134.80	2	125.45
						1	126.33
						0	127.15
					155 $\lambda/2$		145 $\lambda/2$
				157—2	126,28	0—145	118,30
				158—3	126,32	1—146	118.23
						2—147	118.20
						3—148	118.12
						4—149	118.14
						5—150	118.11
	114·80		*119·18*		*126·50*		**118.18**
$\lambda/2 = 2.087$ mm.		$\lambda/2 = 2.091$ mm.		$\lambda/2 = 0.8148$ mm.		$\lambda/2 = 0.815$ mm.	
mean $\lambda/2 = 2.089$ mm.				mean $\lambda/2 = 0.8149$ mm.			
Velocity $= n\lambda$ = **206.46 meters per sec.**				Velocity $= n\lambda$ = **207.09 meters per sec.**			

frequency range, and the average velocity is 202.0 ± 0.05 m./sec. at 97.1°, and 212.6 ± 0.05 m./sec., at 134°. The values given in the International Critical Tables are only up to 100°, at which temperature the value given is too high by about 2 meters. Further experiments will be necessary to establish whether there is any dispersion of velocity at lower and higher frequencies at different temperatures.

TABLE 7

Ethyl Ether 97.1°

Frequency 95 822 Khz				Frequency 94 16 Khz			
n $\lambda/2$	Screw reading mm	↑n $\lambda/2$	Screw reading mm.	n $\lambda/2$	Screw reading mm	↑n $\lambda/2$	Screw reading mm.
		118	6 60	0	5 05	118	4 60
0	7.00	117	7 72	1	6 18	117	5.76
1	8.07	116	8 78	2	7 32	116	6 80
2	9.13	115	9 85	3	8 42	115	7.90
3	10·27	114	10.93	4	9 55	184	9.12
4	11.37	94	32 50	14	20.44	104	20 00
17	25 47	74	54.06	24	31.43	94	31 04
27	36.21	54	75.60	34	42.48	84	42 04
108	123 52	34	97.10	44	53 35	74	52 95
114	129.77	4	129 32	54	64 35	64	63 90
115	130.82	3	130.43	64	75 30	54	74.88
116	131 92	2	131 53	74	86.39	44	85.95
117	133 03	1	132 62	84	97.35	34	96.80
118	134 17	0	133 70	94	108 28	24	107 88
	114 $\lambda/2$		114 $\lambda/2$	104	119.10	14	118 70
114—0	122 77		122 77	114	130.15	14	129 75
115—1	122.75		122.77	115	131 19	3	130 85
116—2	122·79		122.75	116	132 28	2	131.95
117—3	122·76		122 71	117	133 43	1	132.98
118—4	122 80		122.72	118	134 53	0	...
					113 $\lambda/2$		113 $\lambda/2$
				114—1	123 97	114—1	123.86
				115—2	123 87	115—2	124.05
				116—3	123 86	116—3	124 05
				187—4	123 88	117—4	124 01
	122·77₄		*122·74₄*		*123·89₅*		*124·00*
$\lambda/2$ = 1.0769 mm.		$\lambda/2$ = 1.0767 mm.		$\lambda/2$ = 1.0964 mm		$\lambda/2$ = 1.0973 mm.	
mean $\lambda/2$ = 1.0768 mm.				mean $\lambda/2$ = 1 0968 mm.			
Velocity = $n\lambda$ = **206.6 meters per sec.**				Velocity = $n\lambda$ = **206.94 meters per sec.**			

Tables 6, 7 and 8 show the measurements of supersonic velocity in the ethyl ether. Apparently there is no dispersion, the average velocity being 206.6 ± 0.1 at 97.1° and 217.4 ± 0.01 m./sec. at 134°. The values calculated from the formula given in the I. C. T. at these two temperatures are 210.4 and 221.4 m./sec. respectively. The lower values observed in the present investigation cannot be due to dispersion.

TABLE 8

Ethyl Ether 134°

Frequency 93·887 Khz				Frequency 126·238 Khz.			
$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.
		100	12·08	0	11·85		
0	13·48	99	13·18	1	12·60	132	12·35
1	14·65	98	14·38	2	13·40	131	13·20
2	15·78	97	15·48	3	14·30	130	14·03
3	16·90	96	16·55	13	22·95	129	14·90
13	28·55	86	28·55	23	31·55	128	15·72
23	40·10	76	39·80	33	40·23	127	16·60
33	51·70	66	51·00	43	48·75	117	25·23
43	63·28	65	52·60	53	57·38	107	33·90
53	74·87	55	64·18	63	66·05	97	42·45
63	86·42	45	75·70	73	74·60	87	51·08
		35	87·27	83	83·23	77	59·70
73	98·00	25	98·90	93	91·85	67	68·35
83	109·50	15	110·43	103	100·43	56	77·80
93	121·15	5	122·05	113	109·08	46	86·35
103	132·65	4	123·20	123	117·57	36	95·00
		3	124·30	133	126·28	26	103·60
		2	125·50	134	127·08	16	112·25
		1	...	135	127·95	4	122·50
		0	127·75	136	128·84	3	123·40
			94 $\lambda/2$	137	129·70	2	124·20
		2—96	108·95	138	130·60	1	125·07
		3—97	108·82			0	125·90
		4—98	108·82		135 $\lambda/2$		128 $\lambda/2$
	100 $\lambda/2$	5—99	108·87	136—1	116·24	0—128	110·18
103—3	115·75			137—2	116·30	1—129	110·17
				138—3	116·30	2—130	110·17
						3—131	110·20
						4—132	110·15
			108·86		*116·28*		*110·17*
$\lambda/2$ = 1·1575 mm.		$\lambda/2$ = 1·158 mm.		$\lambda/2$ = 0·8613 mm.		$\lambda/2$ = 0·8607 mm.	
mean $\lambda/2$ = 1·15775 mm.				mean $\lambda/2$ = 0·8610 mm.			
Velocity = $n\lambda$ = **217.44 meters per sec.**				Velocity = $n\lambda$ = **217.45 meters per sec.**			

The values for methyl ether (Table 9) were obtained previously in Part II (This Journal, Vol. **21A**, Part XL, pp. 455—465), after correcting for the possible change in frequency difference, which was systematically 1.008 times that assumed.

TABLE 9.

n-Propyl Ether		Methyl Ether.							
97·1°		25°				97·1°			
n	Screw reading mm.	n	Srew reading mm.	n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm
0	4·90	1	2·55	1	135·75	0	12·85	1	141·65
1	7·10	2	5·05	2	133·50	4	23·85	2	138·75
2	8·80	3	7·15	3	131·10	5	26·79	3	136·05
3	10·85	4	10·00	4	128·45	6	29·75	4	133·35
4	12·70	5	12·30	5	125·80	7	32·35	5	130·35
5	14·70	10	24·90	6	123·10	8	35·85	10	116·40
10	24·30	15	37·15	7	120·70	25	82·05	15	102·85
20	43·75	20	49·80	9	118·28	30	95·90	25	85·90
30	62·20	25	62·00	10	115·85	35	109·10	35	48·60
40	82·85	35	86·90	11	113·25	40	122·85	45	20·95
50	102·00	40	98·30	12	110·45	44	134·05	46	18·00
60	121·70	51	126·10	20	90·95	45	137·40	47	15·05
67	135·95	52	128·70	30	64·40	46	139·70	48	12·45
68	137·95	53	131·60	36	49·30	47	142·60	49	9·55
70	141·25	56	138·75	41	39·25	48	145·10	50	6·95
	10 λ/2		51 λ/2		29 λ/2		40 λ/2		45 λ/2
0—10	19·40	52—1	126·15	30—1	71·35	44—4	110·20	46—1	123·65
10—20	19·45	53—2	126·55	36—7	71·40	45—5	110·65	47—2	123·70
20—30	19·45	56—5	126·45	41—12	71·20	46—6	109·95	48—3	123·60
30—40	19·65					47—7	110·25	49—4	123·80
40—50	19·15					48—8	109·25	50—5	123·40
50—60	19·70								
60—70	19·55								
	19·48		*126·38*		*71·32*		*110·06*		*123·63*
λ/2=1·948 mm.		λ/2=2·478 mm. λ/2=2·459 mm. mean λ/2≒2·478 mm.				λ/2=2·751 mm. λ/2=2·747 mm. mean λ/2=2·749 mm.			
Velocity=nλ =194·1m./sec.		Velocity =*n*λ =244.2 m/sec.				Velocity=*n*λ =271·7 m./sec.			
×**1.008=195.6**		**246.2**				**273.9**			

The measurements for normal propyl ether at 97.1° (Table 9) were carried out under the same conditions as the results given in Part II. The velocity is 195.6 m./sec. at 49.42 Khz. in one cm. tube.

Table 10 shows the results of measurements of the velocity in cyclohexane. The average value for the velocity is 191.5 ± 0.3 m./sec. at 97.1° and 202.0 ± 0.3 m./sec. at 134°.

TABLE 10

Cyclohexane

97·1°				134°			
95·82 Khz.		94·16 Khz.		93·889 Khz.		126·264 Khz.	
$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.	$n\ \lambda/2$	Screw reading mm.
0	133·78	0	133·45	0	123·82	0	115·70
1	132·82	1	132·48	2	121·85	1	114·88
2	131·76	2	131·50	3	120·70	2	114·10
3	130·77	3	130·50	4	119·70	4	112·48
13	120·75	4	129·47	5	118·55	5	111·75
23	110·76	5	128·42	15	107·85	6	110·90
33	100·80	15	118·23	25	97·05	16	103·00
43	90·79	35	97·90	35	86·20	26	94·96
53	80·83	55	77·65	45	75·55	36	86·95
63	70·80	75	57·38	55	64·75	46	78·98
73	60·73	95	37·09	65	53·95	56	70·96
83	50·79	115	16·75	75	43·20	66	62·93
93	40·73	123	8·65	85	32·40	76	54·97
103	30·80	124	7·72	95	21·60	86	46·90
113	20·78	125	6·73	96	20·75	96	39·03
123	10·73	126	5·72	97	19·55	106	31·05
124	9·74	127	4·65	98	18·45	107	30·23
125	8·72			99	17·38	108	29·35
126	7·79			100	16·28	109	28·50
127	6·79			101	15·25	110	27·80
128	5·73						
	125 $\lambda/2$		123 $\lambda/2$		96 $\lambda/2$		106 $\lambda/2$
0—125	125·06	0—123	124·80	2—98	103·40	0—106	84·65
1—126	125·03	1—124	124·76	3—99	103·32	1—107	84·65
2—127	124·97	2—125	124·77	4—100	103·42	2—108	84·75
3—128	125·04	3—126	124·78	5—101	103·30	4—110	84·68
	125·03		*124·78*		*103·36*		*84·68*
$\lambda/2$ = 1·0002 mm.		$\lambda/2$ = 1·0145 mm.		$\lambda/2$ = 1·0766 mm.		$\lambda/2$ = 0·7889 mm	
Velocity = $n\lambda$ = **191.68 m./sec.**		Velocity = $n\lambda$ = **191.05 m./sec.**		Velocity = $n\lambda$ = **202.16 m./sec.**		Velocity = $n\lambda$ = **201.73 m./sec.**	

Table 11 shows the measurements in normal hexane vapour, the average velocity being 191.5 m./sec. at 97.1° and 202.0 m./sec. at 134°.

There are no values reported in the literature for the velocity in acetone, methyl ether, propyl ether, cyclohexane and normal hexane.

TABLE 11.

n-Hexane 134°.

Frequency 93·889 Khz.						126·264 Khz.	
n	Screw reading mm.	n	Screw reading mm	n	Screw reading mm.	n	Screw reading mm
0	128·90	0	7·00	0	131·63	0	131·45
1	127·90	1	8·10	1	130·60	1	130·70
2	126·84	2	9·15	2	129·50	2	129·85
3	125·75	3	10·17	3	128·48	3	129·03
4	124·60			12	118·85	4	128·23
5	123·60			23	107·20	25	111·58
45	81·15	41	50·50	42	87·00	46	94·95
65	59·90	61	71·75	62	65·70	67	78·40
85	38·55	81	93·15	92	33·80	91	59·30
105	17·30	101	114·40	102	23·10	137	23·00
106	16·30	102	115·40	114	10·40	138	22·30
107	15·22	103	116·45	115	9·30	139	21·45
108	14·10	104	117·50	116	8·30	141	20·00
109	13·03	105	118·55	117	7·25		
	104 $\lambda/2$		104 $\lambda/2$		114 $\lambda/2$		137 $\lambda/2$
1—105	110·60	104—0	110·50	0—114	121·23	0—137	108·45
2—106	110·54	105—1	110·45	2—116	121·20	1—138	108·40
3—107	110·53			3—117	121·23	2—139	108·40
4—108	110·50						
5—109	110·57						
	110·55		*110·47*		*121·22*		*108·42*
$\lambda/2$ = 1·0630 mm		$\lambda/2$ = 1·0622 mm.		$\lambda/2$ = 1·0633 mm.		$\lambda/2$ = 0·7913 mm,	
mean $\lambda/2$ = 1·0626 mm				Velocity = $n\lambda$ = **196.66 m./sec.**		Velocity = $n\lambda$ = **199.67 m./sec.**	
Velocity = $n\lambda$ = **199.53 m./sec.**							

The values for the velocity of sound in the various vapours are summarised in Table 12.

Calculation of Specific Heats from the Velocity of Sound.

The ratio of specific heats $C_p/C_v = \gamma$ in a gas or vapour is given by the expression $\frac{V^2M}{RT}\,\phi$, where ϕ is given by

$$\phi = 1 - \tfrac{9}{64}\,\pi\,\tau\,(1 - 6\tau^2)$$

in which $\pi = p/p_c$ = actual pressure/critical pressure,

$\tau = T_c/T$ = critical temperature/actual temperature,

TABLE 12.

Dispersion of Supersonic Velocity in Organic Vapours.

	97·1°					134°		
	49·42 Khz.	94·16 Khz.	95·82 Khz.	126·648 Khz.	Average	93·889 Khz.	126·264 Khz.	Average
Acetone ...	238·60	238·60	238·56	238·C0	238·6	251·05	251·15	251 10
Benzene ...	202·18	201·90	202·00	202·05	202·32	221·60	212·71	212·65
Ethyl Ether ...	206·48	206·60	206·60	207·09	206·68	$217{\cdot}4_4$	$217{\cdot}4_5$	$217{\cdot}4_4$
Methyl Ether...	273·9 246·2*	...	...	...	...	...	...	...
Propyl Ether...	195·6	...	...	...	...	...	...	...
Cyclohexane ...	...	$191{\cdot}0_5$	$191{\cdot}6_8$	...	$191{\cdot}3_6$	$202{\cdot}1_6$	$201{\cdot}7_3$	201·9
n-Hexane ...	...	...	...	...	...	$199{\cdot}5_9$	$199{\cdot}6_7$	$199{\cdot}6_5$

* 25°

M is the molecular weight, R is the gas constant expressed in ergs per degree Centigrade (8.3156×10^7) if V is given in cm./sec. The corresponding value of $(C_p - C_v)$ is

$$C_p - C_v = R\ (1 + 27/16\ \pi\ \tau^3).$$

The derivation of the above factors is given by the Berthelot's equation of state. The value of γ for the various vapours was determined from the absolute measurements of the velocity of sound given in Table 12, importance being given to measurements at 95 Khz. These measurements were carried out in a 5 mm. diameter tube, which was many times the wave length, and therefore there was no tube correction required for determining the velocity in the unconfined gas or vapour.

The details of the calculations of the specific heats from the various factors are given in Table 13, and the comparison of the values given in literature, (Landolt Bornstein and International Critical Tables), with those calculated by the method of Bennewitz and Rossner (Z. Phys. Chem. 1938, **B39**, 126 – 44) from the spectroscopic data of the various substances, is given in Table 14. These authors found that the experimental results for specific heats of organic vapours

TABLE 13.

Specific Heats from the Velocity of Sound in Organic Vapours.

	M	p_k	t_k	97.1°						134°					
				V	$\frac{V^2M}{RT}$	ϕ	γ	$C_p - C_v$	C_p	V	$\frac{V^2M}{RT}$	ϕ	γ	$C_p - C_v$	C
Acetone ...	58·06	60·0	237·0	238·6	1·0740	1·0303	1·1065	2·1187	22·01	251·16	1·0840	1.0223	1.1062	2.0851	21.7
Benzene ...	78·08	47·89	288·5	202·0	1·0362	1·0513	1·0894	2·2084	26·92	212·65	1·0444	1.0380	1.0842	2.1528	27.7
Ethyl Ether ...	74·10	35·61	193·8	206·54	1·0271	1·0383	1·0665	2·1595	34·61	217·45	1·0352	1.0288	1.0650	2.1194	34.7
Methyl Ether ...	46·03	53·0	127·1	246·2*	1·1266*	1·0315*	1·162*	2·1257*	15·2*	...	...	...	...	...	..
	„	„	„	273·9	1·1227	1·0155	1·1401	2·0604	16·8	...	...	...	...	...	..
Propyl Ether ...	102·14	31·7	273·0	195·6	1·2491	1·0711	1·3378	2·0716	7·99	...	...	...	...	...	...
Cyclohexane ...	84·13	40·57	281·0	191·36	1·0010	1·0583	1·0596	2·2401	39·83	201·95	1·0143	1.0430	1.0579	2.1760	39.7
n-Hexane ...	86·14	30·0	234·5	...	...	...	...	...	...	199·6	1·1176	1.0439	1.1677	2.1838	15.2

* 25°.

of non-linear molecules containing carbon, hydrogen and oxygen, could be expressed by the equation

$$(C_v)_{p=0} = 3R + \sum_{1} q_i E v_1 + \frac{(3n - 6 - \sum_{1} q_1)}{\sum q_i} \sum q_i E_{\delta_i}$$

where $\sum_{1} q_1 =$ no. of valence bonds in molecule, n = total no. of atoms in molecule, Ev_1 and $E\delta_i$ = Einstein's functions for a given bond with characteristic vibration frequencies, v_1 and δ_1. The numerical value of v for each bond was determined from infra red or light scattering data. The values for δ, were determined empirically from the experimental values of molecular heats for some known substances by a step by step calculation. This equation yielded results in excellent agreement with their own experimental data obtained by the method of continuous flow calorimeter, and with that of other investigators.

The values of the Einstein's functions are given below :—

Bond Molecule	$\frac{v}{\delta}$ -1 cm.	Absolute Temperature.					
		T = 290	330	370	410	450	490
C − C (H_3C-CH_3)	990 390	0·362 1·470	0·513 1·572	0·660 1·647	0·796 1·704	0·921 1·746	1·031 1·784
C − O (Alcohol)	1031 205	0·320 1·824	0·463 1·859	0·606 1·884	0·742 1·902	0·867 1·916	0·979 1·927
C = C ($H_2=CH_2$)	1620 845	0·0426 0·549	1·0867 0·718	1·148 0·871	0·223 1·005	0·308 1·122	0·397 1·222
C = O (Ketone)	1700 390	0·320 1·470	0·0677 1·572	0·119 1·647	0·186 1·704	0·262 1·746	0·345 1·784
C − H (aliphatic)	2920 132	0·0002 0·125	0·0010 0·213	0·0031 0·317	0·0077 0·427	0·0157 0·540	0·2628 0·651
C − H (aromatic)	3050 1320	0·0002 0·125	0·0006 0·213	0·0021 0·317	0·0053 0·427	0·0112 0·540	0·0214 0·651
O − H (H_2O)	3419 1150	0·0001 0·220	0·0002 0·340	0·0006 0·469	0·0018 0·598	0·0043 0·721	0·0089 0·835

It is found that in the case of ethyl ether the contribution of C—O frequencies is one and half times that in alcohol, as determined experimentally from the various values given in the literature, that in methyl ether is the same as in alcohol.

The use of the above table and equation yields $(C_v)_{p=o}$ as a function of temperature. In order to calculate $(C_p)_{p=p}$ the conversion of the two specific heats is made by using the Berthelot's equation of state and the following equation :—

$$(C_p)_{p=p} = (C_v)_{p=o} + R\left[1 + \frac{81}{32} \times \frac{p}{p_c} \times \left(\frac{T_c}{T}\right)^3\right]$$

The results given in Table 14 show the excellence of this formula for finding out the temperature coefficient of specific heats. More elaborate calculations are possible through the work of Mecke and Kohlrausch on the molecular structure, from the eigen frequencies, with the help of Frank Einstein formula. This method, however, leads to very complicated calculations and sometimes the arrangement of the frequencies is not clear in absence of experimental values for the specific heat of the vapour.

TABLE 14.

Comparison of the Specific Heats C_p with those calculated from Spectroscopic data.

Substance	Temp. °C	C_p Obs	C_p Cal	△
Acetone	68	20·1	19·8	+0·3
	97·1	22·0	21·2	+0·8
	103	21·7	21·3	+0·4
	134	21·7	22·7	−1·0
	137	22·5	22·8	−0·3
	181	23·9	24·6	−0·7
Benzene	20	20·1	20·2	−0·1
	74·5	23·3	23·6	−0·3
	80	20·3	23·9	−3·6
	90	25·4	24·6	+0·8
	97·1	26·9	25·0	+1·9
	100	25·8	25·2	+0·6
	107	25·9	25·5	+0·4
	134	27·7	27·1	+0·6
	137	27·5	27·3	+0·2
	167	29·3	29·1	+0·2
	350	38·9	38·3	+0·6
Cyclohexane	97·1	39·8	35·4	+4·4
	100	34·8	35·5	−0·7
	134	39·7	39·6	−0·1
	137	37·5	39·7	−2·2
n.Hexane	134	15·7	39·1	?
	137	39·4	39·2	+0·2

Substance	Temp. °C	C_p Obs.	C_p Cal.	△
Propyl Ether	97·1	8·0	43·8	?
Methyl Ether	25	15·2	16·3	−1·1
	97·1	16·8	17·0	+0·2
Ethyl Ether	35	33·0	29·2	+3·8
	35	27·8	29·2	−1·4
	68	31·7	31·4	+0·3
	97·1	34·6	33·4	+1·2
	100	35·2	33·5	+1·7
	103	34·2	33·7	+0·5
	134	34·7	35·8	−1·1
	137	...	36·0	...
	146	35·6	36·7	−1·1
	185	40·5	39·2	+1·3
	200	41·0	40·3	+0·7
	250	39·5	43·0	−3·5
	300	44·0	46·4	−2·4
	350	44·5	49·8	−5·3

The results at 97° for the various vapours differ appreciably from those calculated, owing to the fact that Berthelot's equation of state does not hold very well for vapours which are not far removed from the saturation point. It is significant to note that the values of specific heats at 97° are systematically higher, as expected. At 134° the specific heats for the vapours of ethyl ether and acetone, are less by 3.5 and 5% respectively than those calculated from the spectroscopic data, which seems to indicate that we are near the dispersion region. This fact was also confirmed by the marked absorption observed at higher frequencies. When allowance is made for these factors, the values of specific heats calculated from supersonic velocity are in very good agreement with those obtained by the spectroscopic method.

Attention is, however, drawn to the serious discrepancy between the calculated and the observed values for *n*-hexane. The vapour of this compound showed a fairly strong absorption at 127 Khz. It appears that the frequencies 94 – 127 Khz., at which the measurements were carried out, represent the dispersion region where the time lag between the rotational and vibrational frequencies occurs.

In the case of *n*-propyl ether there is a complete disappearance of all the vibrational specific heats even at 50 Khz. and measurements were difficult at higher frequencies and temperatures.

Although further work is necessary to confirm this observation it is significant to point out that in the case of *n*-hexane, the contribution of the deformation frequencies (δ) to the specific heat (the calculated value of which is 26.7 cal., and that observed, 23.4 cal.), has disappeared from the adiabatic elasticity of the vapour traversed by sound waves of frequency 94 and 126 Khz. This phenomena and the anisotropic nature of both *n*-hexane and propyl ether molecules, is similar to the case of carbon dioxide, carbon disulphide and nitrous oxide, in which the dispersion observed is accounted for by time lag in the transfer of the energy between the vibrational and other states of the molecule, and in which the observed rise in sound velocity corresponds to the disappearance of the contribution of the deformation oscillations [*cf.* Kneser, Ann. Physik, 1911, **11**, p. 761. Kneser and Zulke, Zeits, f. Physik 1932, **77**, 649]. This point will be briefly discussed in the subsequent parts of this series.

SUMMARY.

Specific heats of the vapours of acetone, benzene, cyclohexane, *n*-hexane, methyl ether, ethyl ether and *n*-propyl ether have been determined by the sound velocity method.

No appreciable dispersion was found over the range of 49.5 – 127 Khz., at 97° and 134°, although a greater increase in sound absorption at higher frequency was observed in some of the vapours.

The values of the molecular heats derived from the observed supersonic velocity, have been compared with those calculated from the spectroscopic data by a semi-empirical formula. In the case of *n*-hexane, there was an apparent disappearance of the deformation vibrational heats, and in the case of *n*-propyl ether, there was a complete absence of the contribution of all the vibrational frequencies to the specific heat. For the remaining substances, the specific heats calculated from the velocity of sound at 49—127 Khz., are in agreement with those obtained by the continuous flow calorimeter, especially at 134°, and with those calculated from spectroscopic data, and it appears that the vibrational heats of most of the vapours, reach equilibrium with other components of the molecular heat, in the frequency range studied.

The results of the present investigation are summarised below :—

	97·1°				134°			
	V	γ	C_p obs.	C_p cal.	V	γ	C_p obs	C_p cal
Acetone	238·6	1·1065	22·0	21·2	$251{\cdot}1_6$	1·1062	21·7	22·7
Benzene	202·0	1·0894	26·9	25·0	$212{\cdot}6_5$	1·0842	27·7	27·1
Ethyl Ether	$206{\cdot}5_4$	1·0665	34·6	33·4	$217{\cdot}4_5$	1·0550	34·7	35·8
Methyl Ether (25°)	273·9 246·2	1·1401 1·1620	16·8 15·2	17·0 16·3	...	...	...	...
Propyl Ether	194·0	1·3378	8·0?	43·8	...	...	...	...
Cyclohexane	$191{\cdot}3_6$	1·0596	39·8	35·4	$201{\cdot}9_5$	1·0579	39·7	39·6
n-Hexane	...	...	...	...	199·6	1·1677	15·2?	39·2

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