

SUPERSONIC VELOCITY IN GASES AND VAPOURS.

PART VI. SPECIFIC HEATS OF THE VAPOURS OF ALCOHOLS AND ETHYL ACETATE.

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INTRODUCTION.

In Part V (This Journal, 1939, **22A**, 19—37) the supersonic velocity in vapours of acetone, benzene, cyclohexane, *n*-hexane, methyl ether, ethyl ether and propyl ether, was measured at 97° and 134°, over a range of 49.5—127 Khz. The specific heats calculated from these measurements were, in most of the cases, in good agreement with the values reported in the literature, and with those calculated from the spectroscopic data. The values at 97° were slightly higher owing to association of the molecules and to the fact that Berthelot's equation of state does not give satisfactory results at this temperature. The slightly lower values for acetone and ethyl ether were ascribed to the influence of the proximity of a dispersive region, which was apparently shown by marked absorption at the higher frequency. In the case of vapours of *n*-hexane there was a disappearance of the contribution of the deformation oscillations to specific heats and in the case of *n*-propyl ether, there was complete disappearance of both the valence and transverse vibrational heats. In both the cases it was apparent that a range of frequency of about 100 Khz. represented definite transitions in the supersonic velocity. It was therefore interesting to find out whether any other organic vapours behaved in the same way.

In the present paper the results of measurements of velocity in methyl alcohol, ethyl alcohol, *iso*-propyl alcohol, *n*-propyl alcohol, *tert*-butyl alcohol and ethyl acetate, have been presented, and the

specific heats derived have been compared with the values given in the literature, and with those calculated from the spectroscopic data, by the method referred to in Part V. It was found that in the case of *iso*-propyl alcohol and *tert*-butyl alcohol, the region of frequency over which the measurements were made, apparently represented one and two transitions, due to disappearance of the share of the transverse, and of both transverse and valence vibrations respectively, from the specific heats, but in the case of other vapours, the agreement was as satisfactory as could be expected on the classical ideas of the equilibrium of different components of the molecular heats.

EXPERIMENTAL.

The apparatus used and the experimental procedure followed was the same as that described in Parts I—V. The results of the wave length measurements are given in detail as before, because there was the usual possibility of miscounting the number of peaks, as in the case of counting bands in the optical interferometer, particularly when the wave lengths were small. No attempt was made to make use of all the readings to get a more accurate value, as the other conditions of the experiments, such as temperature, pressure and the purity of the substances, were not reproducible to an accuracy better than 1 part in 1,000. All the substances were purified by the usual methods and carefully dried and fractionated. The results of the measurements are given in Tables 1—11 and the velocities of the vapours at different frequencies have been summarised in Table 12.

TABLE 1.

Methyl Alcohol 97.1°.

Frequency 49.42 KHz.				Frequency 95.82 KHz.			
n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.
0	6.80	0	3.20	0	130.55	0	6.80
1	10.35	1	6.40	1	128.60	1	8.68
2	13.80	2	10.05	2	126.90	2	10.45
3	17.00	3	13.65	3	125.28	3	12.08
4	20.30	4	17.00	4	123.45	4	13.98
5	23.55	5	20.15	14	105.55	14	31.57
15	57.50	15	54.35	24	88.20	24	48.80
25	91.83	25	88.30	34	70.90	36	70.10
26	95.30	26	91.80	44	35.98	46	87.30
27	98.40	27	95.30	54	58.98	56	104.83
28	101.10	28	98.80	64	18.49	66	122.30
29	105.50	30	105.40	70	7.75	70	129.30
30	108.70	31	108.70	11	5.98	71	131.03
31	112.05	32	112.20	72	4.88	72	132.85
29-1	28 $\lambda/2$ 95.15	31-3	28 $\lambda/2$ 95.05	1-71	70 $\lambda/2$ 122.62	70-0	70 $\lambda/2$ 122.50
31-3	95.05	32-4	95.20	2-72	122.52	71-1	122.35
	95.10		95.12		122.57	72-2	122.40
							122.12
$\lambda/2 = 3.3967$ mm.		$\lambda/2 = 3.3967$ mm.		$\lambda/2 = 1.751$ mm.		$\lambda/2 = 1.749$ mm.	
mean $\lambda/2 = 3.3967$ mm.				mean $\lambda/2 = 1.750$ mm.			
Velocity = $n\lambda$ = 335.7 m./sec.				Velocity = $n\lambda$ = 335.4 m./sec.			

There is apparently no dispersion in methyl alcohol vapour. The values for the velocity, however, are quite different from those given in the literature. The average value of the velocity at 97.1° is 335.4 m./sec. and at 134°, 352.5 m./sec.

In ethyl alcohol the average value of the velocity at 97° is 269.5 m./sec., and at 134°, 284.4 m./sec. and the result is in agreement with the Jaeger's (1889) and Dixon's values, the other results reported in literature being too high.

In the case of *iso*-propyl alcohol the velocity at 126.5 KHz., is less by 1.2 meters than the value 255.4 m./sec. at 97°, at 49 and 94 KHz.

TABLE 2.

Methyl Alcohol 97.1°

Frequency 94.16 KHz.			
<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.
0	124.10	0	5.90
1	122.73	1	7.73
2	120.92	2	9.40
3	119.08	3	11.45
13	101.43	13	29.00
33	65.65	23	46.80
43	47.90	33	64.65
53	30.20	43	82.20
63	12.15	53	100.05
64	10.50	63	118.08
65	8.63	71	132.80
66	6.85	72	133.80
67	5.20	73	135.67
	$64 \lambda/2$		$70 \lambda/2$
65-1	114.12	71-1	124.62
66-2	114.07	72-2	124.40
67-3	113.88	73-3	124.15
	144.02		124.51
$\lambda/2 = 1.7815$ mm		$\lambda/2 = 1.7778$ mm.	
Mean $\lambda/2 = 1.780$ mm.			
Velocity = $n \lambda$ = 335.23 m./sec.			

At 134°, measurements could be obtained only at 94 KHz., at which the velocity is 270.2 m./sec. Measurements at 126 KHz. at 134° could not be obtained owing to absorption.

In the case of *n*-propyl alcohol, the average value for the velocity at 134° is 244.5 m./sec. The absorption in *n*-propyl alcohol was not so marked as in *iso*-propyl alcohol.

The velocity in *tert*-butyl alcohol is 225.6 m./sec. at 134°, at 93.889 KHz., no measurements being possible at the higher frequency owing to absorption.

TABLE 3.
Methyl Alcohol 134.°

Frequency 93.889 Khz.				Frequency 126.264 Khz.			
"	Screw reading mm	"	Screw reading mm.	"	Screw reading mm.	"	Screw reading mm.
0	133.05	0	4.47	0	134.00	0	4.55
1	131.45	1	6.47	1	132.65	1	6.15
2	129.40	2	8.03	2	131.30	2	7.44
3	127.55	3	13.17	4	128.45	3	9.00
4	125.42	4	11.85	12	117.55	14	24.48
5	123.95	5	13.55	22	103.53	24	38.53
6	122.12	6	15.55	32	89.40	35	53.75
16	103.10	7	17.60	45	71.55	45	67.78
26	84.45	17	36.33	55	57.50	55	81.68
36	65.75	27	55.22	65	43.20	65	95.50
46	46.92	37	73.65	75	29.65	75	109.80
56	28.95	47	92.55	85	15.75	85	123.58
66	9.35	57	111.27	86	14.15	86	125.10
68	5.68	67	130.12	87	12.83	87	126.50
69	3.65	68	132.10	89	10.20	86	128.00
	50 $\lambda/2$		62 $\lambda/2$		85 $\lambda/2$		85 $\lambda/2$
0-66	123.70	67-5	116.57	0-85	118.25	85-0	119.03
2-68	123.72	68-6	116.56	1-86	118.50	86-1	118.95
3-69	123.70			2-87	118.47	87-2	119.06
	123.70		116.56	4-89	118.25	88-3	119.00
					118.37		119.01
$\lambda/2 = 1.874$ mm.		$\lambda/2 = 1.880$ mm.		$\lambda/2 = 1.393$ mm.		$\lambda/2 = 1.400$ mm.	
Mean $\lambda/2 = 1.877$ mm.				Mean $\lambda/2 = 1.396$ mm.			
Velocity = $n\lambda$ = 352.46 m./sec.				Velocity = $n\lambda$ = 352.6 m./sec.			

TABLE 4.

Ethyl Alcohol 97.1°

Frequency 49.42 KHz.				Frequency 95.82 KHz.			
<i>n</i>	Screw reading mm	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm
0	1.70	0	1.60	0	133.93	0	5.40
1	4.70	1	4.70	1	132.55	2	8.06
2	7.20	2	7.35	2	131.05	3	9.50
3	10.10	3	10.08	3	129.63	4	10.96
4	12.70	4	12.57	16	111.75	14	25.32
5	15.55	5	15.60	26	97.42	24	40.05
15	42.70	15	43.15	36	83.25	36	55.98
25	70.20	25	70.30	47	68.10	46	70.28
33	92.28	35	97.75	57	53.85	57	85.35
34	94.95	36	100.48	68	38.25	67	99.48
35	97.70	37	103.20	79	23.30	77	114.00
36	100.34	38	106.00	89	8.93	89	130.12
37	103.18	39	108.68	90	7.43	90	131.70
38	105.75	40	111.30	91	6.10	91	133.03
				92	4.78	92	134.50
	35 $\lambda/2$		35 $\lambda/2$		88 $\lambda/2$		88 $\lambda/2$
36-1	95.64	56-1	95.78	1-89	123.62	90-2	123.64
37-2	95.58	37-2	95.85	2-90	123.62	91-3	123.53
38-3	95.65	38-3	95.94	3-91	123.53	92-4	123.54
	95.62	40-5	95.70		123.59		125.57
			95.87				
$\lambda/2 = 2.732$ mm.		$\lambda/2 = 2.7347$ mm.		$\lambda/2 = 1.4043$ mm.		$\lambda/2 = 1.4043$ mm.	
mean $\lambda/2 = 1.7374$ mm.				mean $\lambda/2 = 1.4043$ mm.			
Velocity = $n\lambda$ = 270.28 m./sec.				Velocity = $n\lambda$ = 238.12 m./sec.			

In the case of ethyl acetate at 97° and 96 KHz., the value of the velocity is 189.3 m./sec., the value at 134° being 198.8 m./sec. No measurements were possible at higher frequencies on account of absorption. The value at 76° reported by Lechner (1909) is too high.

Calculation of Specific Heats from the Velocity of Sound.

The specific heats have been calculated from the values of the velocity of sound in the various organic vapours, by the same procedure which was adopted in Part V. The results are shown in Table 13.

TABLE 5

Ethyl Alcohol 97.1°

94.16 Khz.		126 648 Khz.			
<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.
0	132.75	0	134.30	0	5.20
1	131.35	1	133.24	1	6.18
2	129.93	2	132.15	2	7.23
3	128.46	3	131.08	3	8.38
4	127.00	4	130.01	4	9.44
14	112.75	14	119.40	14	20.02
24	98.35	34	98.05	34	41.25
34	84.15	45	86.45	44	51.74
44	69.90	55	75.69	54	62.58
54	55.45	65	65.18	84	94.32
64	41.20	85	43.90	94	105.00
74	26.85	96	32.28	104	115.65
84	12.53	106	21.55	114	126.13
85	11.15	116	11.22	119	131.53
86	9.63	117	9.93	120	132.52
87	8.20	118	8.86	121	133.62
88	6.72	119	7.85	122	134.70
	$84 \lambda/2$		$116 \lambda/2$		$120 \lambda/2$
0-84	120.22	0-116	123.28	120-0	127.32
1-85	120.20	1-117	123.31	121-1	127.44
2-86	120.30	2-118	123.29	122-2	127.47
3-87	120.26	4-119	123.23		
	120.25		123.28		127.41
$\lambda/2=1,4315 \text{ mm.}$		$\lambda/2=1,0627 \text{ mm.}$		$\lambda/2=1,0617 \text{ mm}$	
Velocity = $n \lambda$ = 269.6 m./sec.		Mean $\lambda/2=1,0622 \text{ mm.}$			
		Velocity = $n \lambda$ = 269.1 m./sec			

The specific heats have also been calculated from the spectroscopic data by the method of Bennewitz and Rossner (*vide infra*) at different temperatures, and the calculated values have been compared with those observed in the present investigation, and also with those which are given in Landolt Bornstein and International Critical Tables. The results are given in Table 14.

The accuracy of the results obtained in the present investigation may be illustrated by the fact that a difference of 0.5% in the value of

TABLE 6

Ethyl Alcohol 134°

Frequency 93-889 Khz.				Frequency 126-264 Khz.			
"	Screw reading mm.	"	Screw reading mm.	"	Screw reading mm.	"	Screw reading mm.
0	7.23	0	132.25	0	133.15	0	5.38
1	8.68	1	130.68	1	131.96	1	6.42
2	10.20	2	129.23	2	130.80	2	7.38
3	11.70	3	127.75	3	129.65	3	8.48
13	27.10	14	111.00	13	118.50	14	21.12
23	42.23	24	95.95	24	106.10	24	32.25
33	57.25	34	80.95	34	94.90	34	43.60
43	72.38	44	65.60	44	83.48	45	55.80
53	87.50	54	50.38	54	72.30	55	67.30
63	102.62	64	35.40	64	61.00	65	78.35
75	120.80	79	12.60	75	48.60	75	89.75
76	122.37	80	11.13	85	37.35	85	101.12
77	123.88	81	9.55	105	14.75	105	123.37
78	123.53	82	8.12	106	13.60	106	124.50
79	126.85	83	6.60	107	12.43	107	125.37
80	128.26	84	5.10	108	11.35	108	126.68
	$77 \lambda/2$		$80 \lambda/2$		$104 \lambda/2$		$104 \lambda/2$
77-0	116.55	0-80	121.12	1-105	117.21	105-1	117.09
78-1	116.55	1-81	121.12	2-106	117.20	106-2	117.12
79-2	116.55	2-82	121.11	3-107	117.22	107-3	117.09
	116.55		121.12		117.21		117.10
$\lambda/2 = 1.5149$ mm.		$\lambda/2 = 1.5141$ mm.		$\lambda/2 = 1.127$ mm.		$\lambda/2 = 1.126$ mm.	
mean $\lambda/2 = 1.5145$ mm.				mean $\lambda/2 = 1.1265$ mm.			
Velocity = $n\lambda$ = 284.98 m./sec.				Velocity = $n\lambda$ = 284.47 m./sec.			

ϕ (the correction for the compressibility) will account for 1.4 cal. difference between the observed and the calculated value for the molecular heats of *n*-propyl alcohol, and that a difference of 1 part in 2000 in the velocity of sound in ethyl acetate vapour, will cause a change of 0.5 cal. in the molecular heat. The maximum deviations observed in the case of most of the vapours are within the above two limits, the probable error being of the order of 0.5 calorie. It is therefore obvious that Berthelot's equation of state holds very well for all the substances under the conditions of the experiment. In order to obtain

TABLE 7

Iso-Propyl Alcohol 97.1°

Frequency 49.42 KHz.				Frequency 95.82 KHz.			
n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.
0	10.55	0	129.25	0	134.00	0	5.48
1	13.35	1	126.65	1	132.75	1	7.00
2	16.00	2	124.05	2	131.58	2	8.35
3	18.35	4	120.20	3	130.10	3	9.54
4	21.10	5	102.75	13	116.80	4	10.98
14	45.00	15	77.75	22	104.63	14	24.26
24	72.25	25	52.90	33	90.10	24	37.68
34	97.30	35	27.85	43	76.63	34	51.03
44	124.85	45	13.10	53	63.55	44	64.28
45	127.23	46	10.60	63	50.05	54	77.57
46	129.85	47	8.05	73	36.50	74	104.34
				93	10.18	94	130.94
	43 $\lambda/2$		45 $\lambda/2$	94	9.03	95	132.30
44-1	111.50	45-0	116.15	95	7.28	96	133.40
45-2	111.23	46-1	116.05	96	6.35	97	134.92
46-3	111.50	47-2	116.05	97	5.00	98	136.26
				94 $\lambda/2$			94 $\lambda/2$
				1-95	123.47	94-0	125.46
				2-96	125.23	95-1	125.30
				3-97	125.10	96-2	125.02
						97-3	125.38
						98-4	125.28
	111.41		116.03		125.27		125.29
$\lambda/2=2.591$ mm		$\lambda/2=2.579$ mm.		$\lambda/2=1.3326$ mm.		$\lambda/2=1.3328$ mm	
mean $\lambda/2=2.585$ mm.				mean $\lambda/2=1.3327$ mm.			
Velocity = $n \lambda$ = 255.5 m./sec.				Velocity = $n \lambda$ = 255.4 m./sec.			

more accurate molecular heats, it is essential to attain a still higher accuracy, which the supersonic interferometer is capable of, and pay special attention to purity of compounds and define other physical conditions such as uniformity of temperature, pressure, etc., very closely. The author has already demonstrated the possibility of obtaining a high accuracy in the measurement of the absolute frequency of the quartz oscillators by means of a simple and inexpensive apparatus in Part IV

TABLE 8.

Iso-Propyl Alcohol

97.1

134.

94.16 KHz.		126 r+8 KHz		Frequency 93.889 KHz			
n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.
0	5.97	0	134.16	0	7.78	0	132.50
1	7.31	1	133.19	1	9.15	1	131.05
2	8.65	2	132.27	2	10.52	2	129.65
3	10.34	3	131.05	3	11.94	3	128.20
4	11.15	4	130.10	14	27.85	13	113.77
25	39.92	24	110.10	24	42.15	23	99.35
45	67.15	44	90.00	34	56.48	33	85.00
55	80.70	64	70.00	44	70.98	43	70.58
65	93.90	84	50.00	54	85.50	53	56.05
75	107.80	104	29.50	64	98.80	63	41.81
85	121.20	124	9.55	74	114.30	73	27.37
92	130.63	126	7.62	84	128.64	84	11.64
93	132.06	127	6.85	85	130.10	85	10.22
94	133.41	128	5.85	86	131.50	86	8.85
95	134.81	129	4.65	87	132.95	87	7.42
	92 $\lambda/2$		126 $\lambda/2$		84 $\lambda/2$		84 $\lambda/2$
0-92	124.66	0-126	126.54		84 $\lambda/2$		84 $\lambda/2$
1-93	124.75	1-127	126.34	84-0	120.86	0-84	120.86
2-94	124.76	2-128	126.42	85-1	120.95	1-85	120.83
3-95	124.47	3-129	126.36	86-2	120.98	2-86	120.80
				87-3	121.01	3-87	120.78
	124.76		126.42		120.95		120.82
$\lambda/2 = 1.356$ mm.		$\lambda/2 = 1.0033$ mm		$\lambda/2 = 1.4399$ mm.		$\lambda/2 = 1.4383$ mm.	
Velocity = $n\lambda =$ 295.36 m./sec.		Velocity = $n\lambda =$ 294.13 m./sec		mean $\lambda/2 = 1.4391$ mm.			
				Velocity = $n\lambda$ = 270.23 m./sec.			

of this series. It is also possible to attain a higher accuracy in the values of the wave lengths by a more elaborate method than averaging.

It will be seen that the observed and the calculated values are in agreement within the limits of experimental error, except in the case of *iso*-propyl alcohol and *tert*-butyl alcohol. In the case of the former,

TABLE 9.

n-Propyl Alcohol 134°.

Frequency 93.889 Khz.				Frequency 126.264 Khz.			
<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.
0	131.10	0	8.10	0	88.30	0	15.30
1	130.00	1	9.40	13	76.30	9	23.95
2	128.65	2	10.38	61	29.25	18	32.95
3	127.40	3	12.05	62	28.15	48	62.20
4	126.18	4	13.30	63	27.55	70	83.80
34	85.55	24	39.50	64	26.50	91	103.30
54	59.35	44	65.40	65	25.35	113	124.85
64	46.55	64	91.40	66	24.50	116	127.70
86	17.90	84	117.48	67	23.55	117	128.70
87	16.60	93	129.10				
88	15.30	94	130.45				
89	13.95	95	131.60				
	86 $\lambda/2$		93 $\lambda/2$	Mean	$\lambda/2$	Mean	$\lambda/2$
0-86	113.20	93-0	121.00	67 $\lambda/2$	0.9664	113 $\lambda/2$	0.9694
1-87	115.40	94-1	121.05	" 66 "	9666	" 107 "	.9696
2-88	113.35	95-2	121.22	" 65 "	.9684		
3-89	113.45			" 64 "	.9656		
	113.35		121.09		0.9670		0.9695
$\lambda/2=1.303$ mm.		$\lambda/2=1.302$ mm.		$\lambda/2=0.9670$ mm.		$\lambda/2=0.9695$ mm.	
mean $\lambda/2=1.3025$ mm				mean $\lambda/2=0.9683$ mm.			
Velocity= $n\lambda$ =244.53 m/sec.				Velocity= $n\lambda$ =244.52 mm			

the specific heat observed is very nearly that due to translational, rotational and valence vibrational energy, and indicates the complete disappearance of all the transverse vibrational energy. *Tert*-butyl alcohol seems to have lost the contribution to the specific heats from the deformational frequencies. It is interesting to point out that the behaviour of these two substances is similar to that of propyl ether and *n*-hexane reported in the previous part.

The substances exhibiting the abnormally low molecular heats are highly anisotropic like CO₂, or possess quasi-tetrahedral structure

TABLE 10
Tert Butyl Alcohol 134°.

Frequency 93.889 KHz.			
"	Screw reading mm.	"	Screw reading mm.
0	8.75	0	128.90
1	9.90	1	127.70
2	11.20	2	126.60
22	35.35	3	125.45
42	59.45	88	23.55
63	84.75	89	22.40
83	108.85	90	21.15
93	120.85	91	19.90
95	123.20	92	18.70
96	124.50	93	17.60
97	125.60	95	15.40
	95 $\lambda/2$		90 $\lambda/2$
95--0	114.45	0--90	107.75
96--1	114.60	1--91	107.80
97--2	114.40	2--93	107.90
		3--93	107.85
	114.48		107.83
$\lambda/2 = 1.205$ mm		$\lambda/2 = 1.198$ mm.	
Mean $\lambda/2 = 1.2015$ mm.			
Velocity = $n \lambda$ = 225.61 m/sec.			

of the type AXB₃. It will be shown in the next part that chloroform, which comes under the latter category, also shows diminution of specific heat. It appears therefore that most of the rotational energy is utilised in 'spinning the top' under the high frequency compressional waves, thus producing the remarkably high absorption of sound energy.

Supersonics in relation to molecular structure.

The remarkable divergence in the values of the specific heats deduced from the supersonic velocity, and those obtained by the calorimetric method or by calculations from spectroscopic data, in the case of some of the vapours, can now be explained on the basis of failure

TABLE 11
Ethyl Acetate

97.1°								134°					
49.42 Khz.				95.82 Khz.				93.889 Khz.					
<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.	<i>n</i>	Screw reading mm.		
0	130.45	0	7.00	0	135.30	0	4.65	0	132.10	0	11.50		
1	128.45	1	9.00	2	133.40	1	5.58	1	131.05	1	12.70		
2	126.40	2	10.45	3	132.45	2	6.66	2	130.15	2	13.90		
3	124.60	12	29.55	4	131.58	3	7.71	4	128.10	4	15.30		
14	101.60	22	49.05	5	130.48	4	8.72	102	24.25	111	128.00		
24	85.05	32	68.05	6	129.47	5	9.72	103	23.18	112	130.45		
34	65.85	42	87.35	16	119.50	6	10.74	104	21.10	113	131.40		
44	45.95	52	106.30	26	109.67	26	30.60	115	1.45	114	182.45		
54	27.75	62	125.50	46	90.60	46	50.32	116	1.36	115	133.35		
65	8.89	64	129.00	86	50.45	86	89.88	117	8.40				
65	6.95	65	131.10	126	10.91	126	129.22	118	7.0				
56	4.95	65	133.00	130	7.10	130	133.37						
				131	6.10	131	134.14						
				132	5.12	132	135.12						
				133	4.15	133	136.15						
	64 $\lambda/2$		64 $\lambda/2$		130 $\lambda/2$		130 $\lambda/2$		116 $\lambda/2$		113 $\lambda/2$		
0-64	121.65	64-0	112.60	0-130	128.20	130-0	128.42	0-116	122.74	113-0	119.90		
1-65	121.55	63-1	122.10	2-132	128.28	131-1	128.56	1-117	122.65	114-1	119.75		
2-66	121.45	66-2	122.05	3-133	128.30	132-2	128.56	2-118	122.85	115-2	119.45		
						133-3	128.44						
	121.55		122.05		128.26		128.50		122.75		119.70		
$\lambda/2 = 1.899$ mm.			$\lambda/2 = 1.907$ mm.			$\lambda/2 = 0.987$ mm.		$\lambda/3 = 0.988$ mm.		$\lambda/2 = 1.0582$ mm.		$\lambda/2 = 1.0593$ mm.	
Mean $\lambda/2 = 1.903$ mm				Mean $\lambda/2 = 0.9875$ mm.				Mean $\lambda/2 = 1.0588$ mm.					
Velocity = $n\lambda$ = 188.1 m./sec.				Velocity = $n\lambda$ = 189.25 m./sec.				Velocity = $n\lambda$ = 188.82 m./sec.					

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	93.899 Khz.	126.264 Khz.	Average
Methyl Alcohol ...	335.7	335.2 ₈	335.4	...	335.4 ₃	352.4 ₈	352.6	352.5 ₉
Ethyl Alcohol ...	270.2 ₈	269.6	269.1 ₂	269.1	269.5 ₂	284.3 ₈	284.4 ₇	284.4 ₂
Iso-Propyl Alcohol ...	255.5	255.3 ₈	255.4	254.1 ₈	255.1	270.2 ₈	...	270.2 ₈
n-Propyl Alcohol	244.5 ₈	244.5 ₂	244.5 ₂
Tert-Butyl Alcohol	225.6 ₁	...	225.6 ₁
Ethyl Acetate ...	188.1	...	189.2 ₈	...	189.2 ₉	198.8 ₂	...	198.8 ₂

of a part of the heat capacity to follow the adiabatic cycle of the supersonic wave. Although further speculation must be reserved until the measurements are extended over a larger frequency range, some *ad hoc* explanation might be given on the basis of the theories on the number of vibration and rotation states in the molecules. Speculations of this type are now possible because of a knowledge of the contribution of different components of the molecule to the specific heat.

Bennewitz and Rossner (*Z. Physik Chem.* 1938, **B.39**, 126-44) in a comprehensive research on specific heats of organic vapours, developed a semi-empirical formula for calculating C_p at different temperatures, based on valence and deformation frequencies determined from vibrational infra-red or Raman Spectra. The results of such calculations were in good agreement with their own measurements by the streaming method. The contribution of deformation oscillation to specific heat were deduced empirically.

TABLE 13.
Specific Heats from the Velocity of Sound in Organic Vapours.

	M	ρ_k	t_k	97.1°						134°					
				V	$\frac{V^2 M}{RT}$	ϕ	γ	$C_p - C_v$	C_p	V	$\frac{V^2 M}{RT}$	ϕ	γ	$C_p - C_v$	C_p
Methyl Alcohol ...	32.04	78.5	210.0	335.3	1.1700	1.0235	1.1975	2.0920	12.68	352.5	1.1763	1.0174	1.1568	2.0656	12.56
Ethyl Alcohol ...	46.06	62.96	213.1	269.3	1.0854	1.0360	1.1179	2.1187	20.08	284.42	1.1009	1.0209	1.1239	2.0848	18.91
Iso-Propyl Alcohol ...	60.08	53.1	234.6	255.4	1.2733	1.0336	1.3159	2.1349	8.89	270.23	1.2963	1.0248	1.3285	2.0997	8.49
n-Propyl Alcohol ...	60.08	50.16	263.7	244.55	1.0613	1.0314	1.0946	2.1272	24.61
Tert-Butyl Alcohol ...	74.10	31.7	234.9	225.6	1.1143	1.0416	1.1607	2.1722	15.69
Ethyl Acetate ...	88.08	38.0	250.1	189.25	1.0250	1.0496	1.0758	2.2116	31.39	198.8	1.0287	1.0382	1.0680	2.1595	33.9

TABLE 14.

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

Substance	Temp. °C	C_p			Substance	Temp. °C	C_p		
		Obs	Cal.	Deviation			Obs	Cal.	Deviation
Methyl Alcohol	77	12.5	13.1	-0.6	n Propyl Alcohol	134	24.6	26.0	-1.4
	97.1	12.7	13.4	-0.7		137	26.9	26.5	+0.4
	134	12.6	14.1	-1.5	Iso Propyl Alcohol	97.1	8.9	24.2	-15.3
	137	14.0	14.1	-0.1		134	8.5	26.0	-17.5
	162	14.7	14.5	-0.2		137	26.6	26.1	+0.5
Ethyl Alcohol	90	18.7	18.4	+0.3	Tert Butyl Alcohol	134	15.7	30.0	-14.3
	97.1	20.1	18.6	+1.5		Ethyl Acetate	73	29.7	29.5
	134	18.9	19.9	-1.0	97.1		31.4	30.9	+0.5
	137	19.8	20.1	-0.3	112		32.7	31.8	+0.9
	164	20.9	21.0	-0.1	134		33.9	33.1	+0.8
	350	28.2	27.1	+1.1	137	33.7	33.3	+0.4	
					167	35.3	35.2	+0.1	

The molecular heats of polyatomic gases are given by the expression.

$$C_p = \frac{3}{2}R \text{ (translation)} + \frac{3}{2}R \text{ (rotation)} + R \text{ (for } C_p - C_{v,1}) \\ + \sum q_i C_{v_i} \text{ (valence vibration)} + \sum q_i C_{\delta_i} \text{ (deformation vibration)}$$

where C_{v_i} and C_{δ_i} are Einstein functions with the characteristic temperatures θ .

In order to illustrate the method, the heat capacity of the vapours of *iso*-propyl alcohol at 97.1° will be calculated. The structural formula for *iso*-propyl alcohol shows twelve atoms ($n=12$) and eleven bonds ($\Sigma q_1=11$) which are of the type, (7) C-H, (2) C-C, (1) C-O and (1) O-H. Taking the values for the valence and deformation vibrations which are given in Part VI, the following summations are obtained:—

	Valence vibrations	Deformation vibrations
(7) C-H	$7 \times 0.0031 = 0.0217$	$7 \times 0.317 = 2.219$
(2) C-C	$2 \times 0.660 = 1.320$	$2 \times 1.647 = 3.294$
(1) C-O	$1 \times 0.606 = 0.606$	$1 \times 1.884 = 1.884$
(1) O-H	$1 \times 0.0006 = 0.0006$	$1 \times 0.469 = 0.469$
	$\Sigma_1 q_1 E_{v_1} = 1.948$	$\Sigma_1 q_1 E_{\delta_1} = 7.886$

$$\frac{(3n-6-\Sigma q_1)}{\Sigma_1 q_1} \Sigma_1 q_1 E_{\delta_1} = \frac{19}{11} \times 7.886 = 13.58.$$

On the basis of complete equilibrium in the various degrees of freedom in the molecule, the molecular heat at atmospheric pressure at 97° comes to 24.2 calories, as against 8.9 observed.

For rotational heat capacity, it is usual to assume the classical values. It will be shown presently that this does not hold in supersonic waves in molecules of AXB₃ type such as in the case of *iso*-propyl alcohols H-C-OH(CH₃)₂. The rotation of the molecules along the CH axis, owing to the high moment of inertia, will cause the disappearance of two degrees of rotation equivalent to R calories, as the molecule is approximately equally loaded. Such a rotation of the molecule will diminish the contribution of the transverse vibrations of all the linkages except that of the CH group of the secondary alcohol. The observed specific heat of *iso*-propyl alcohol on this

basis is made up of, $\frac{3}{2}R$ (translation), $\frac{1}{2}R$ (rotation), R for $C_p - C_v$, 1.948 for valence vibrations and 0.547 for C-H deformation. The total value at 97° (along with 0.16 calorie for change to atmospheric pressure) comes to 8.77 calories as compared with 8.99 observed, the agreement being remarkably good. It must be mentioned that the numerical value of the contribution of valence vibration is nearly the same as that of the two rotational states. It is, however, more plausible to assume the disappearance of the two rotational states from adiabatic supersonic waves, to account for the partial loss of the share of transverse oscillations. Similar conclusions apply to the value at 134° .

The observed diminution in specific heat, is constant over a range of frequencies from 49 to 127 KHz. at both 97° and 134° and is not due, therefore, to the dispersive region, but to a definite transition in the supersonic velocity.

In the case of tertiary butyl alcohol, as the molecule is not symmetrically loaded, the rotational specific heat will degrade to $\frac{2}{3}R$. The following calculations show the contribution of various oscillations to the specific heat at 134° ($n = 15$, $\sum q_i = 14$).

	Valence Vibrations	Deformation Vibrations
9 C-H	$9 \times 0.0074 = 0.0666$	$9 \times 0.420 = 3.780$
3 C-C	$3 \times 0.7860 = 2.3580$	$3 \times 1.700 = 5.100$
1 C-O	$1 \times 0.7320 = 0.7320$	$1 \times 1.900 = 1.900$
1 O-H	$1 \times 0.0017 = 0.0017$	$1 \times 0.588 = 0.588$
$\sum q_i E v_i = 3.1580$		$(3n - 6 - \sum q_i) = 11.368$
		$\frac{(3n - 6 - \sum q_i)}{\sum q_i} \sum q_i E v_i = \frac{11}{14} \times 11.368 = 20.3$

The contribution of the deformation vibrations to specific heat is thus 20.3 calories at 134°. But as the transverse vibrations in the three sets of groups will be inoperative when the molecule is rotating on each of the axis C—OH, C—CH₃, etc., the contribution of these oscillations to specific heat will be only one-fourth of the calculated, namely, 5.1 calories. The observed specific heat of *tert*-butyl alcohol, is thus composed of, $\frac{3}{2} R$ (translation), $\frac{3}{2} R$ (rotation), R (2.172) for $C_p - C_v$, 3.16 for the valence vibration, and only 5.1 calories, the share of the deformation oscillation; total (along with 0.28 calories as the correction for atmospheric pressure) comes to 15.68 calories as compared with 15.7 calories deduced from the supersonic velocity. The agreement is remarkably good and fortuitous, considering the various assumptions made.

In the *n*-hexane investigated in Part V, the share of the transverse oscillations to the specific heat is 26.7 calories, while the discrepancy is 23.4 calories. It is therefore obvious that a part of the transverse oscillations participate in the specific heat. If the six end C—H groups, which are most free to vibrate, remain active, they will absorb 4.7 calories. As the molecule is highly anisotropic, it may remain oriented with its length in the direction of the supersonic radiation, and it will lose one degree of rotational freedom corresponding to $\frac{R}{2}$. The calculated specific heat then comes to 16.2 calories as compared with 15.7 calories derived from supersonic velocity.

In the case of propyl ether it is obvious that even a frequency of 50 Khz. is too high for any of the vibrations to participate in the specific heat. The observed value is therefore due to translation and rotation only.

SUMMARY.

The supersonic velocity in the vapours of methyl alcohol, ethyl alcohol, *iso*-propyl alcohol, *n*-propyl alcohol, *tert*-butyl alcohol and that of ethyl acetate have been measured at 97 and 134° over a frequency range of 49—127 Khz. There was apparently no dispersion over this frequency range, although in the case of *iso*-propyl

alcohol and *tert*-butyl alcohol, there was a strong absorption evident at the higher frequency and higher temperature.

The specific heats deduced from the observed velocities have been compared with those calculated from the spectroscopic data and were found to be in fair agreement, except in the case of *iso*-propyl alcohol and *tert*-butyl alcohol. It is interesting to note that both these molecules are of AXB₃ type. The discrepancy in the molecular heats in the above compounds and in *n*-hexane has been quantitatively accounted for on the basis of partial disappearance of the share of rotational and deformation oscillations.

Berthelot's equation of state has been found to hold very well in the case of the vapours.

The results of the present investigation are summarised in the following table :—

	97.1°.				134°.			
	V	γ	C _p		V	γ	C _p	
			obs.	cal.			obs.	cal.
Methyl Alcohol	335.3	1.1975	12.7	13.4	352.5	1.1968	12.6	14.1
Ethyl Alcohol ...	269.1	1.1137	20.1	18.6	284.4	1.1200	18.9	19.9
<i>Iso</i> -Propyl Alcohol ...	255.4 ₄	1.3159	8.9	8.77	270.2 ₃	1.3285	8.5	(26.0)
<i>n</i> -Propyl Alcohol	244.5 ₃	1.0946	24.6	26.0
<i>Tert</i> -Butyl Alcohol	225.6	1.1607	15.7	15.68 } (33.1)
Ethyl Acetate ...	189.2 ₅	1.0758	31.4	30.9	198.8	1.0484	33.9	33.1

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