SUPERSONIC VELOCITY IN GASES AND VAPOURS.

PART VII. SPECIFIC HEATS OF THE VAPOURS OF DICHLOROMETHANE, CHLOROFORM, CARBON TETRACHLORIDE & ETHYLENE DICHLORIDE

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INTRODUCTION.

In Parts V and VI (This Journal, 1939, **22A**, 19, 39) it was shown that the supersonic velocity in several organic vapours in the range of 50 – 127 Khz. at 97 and 134°, showed no appreciable dispersion, although increase in sound absorption with frequency was observed. In the case of the vapours of *n*-hexane, propyl ether, *iso*-propyl alcohol and *tert*-butyl alcohol, the absorption was appreciable, and the measurements at 50 and 94 Khz., gave velocities which were in agreement with either complete disappearance of all the vibrational specific heats or, only of those that were contributed by the transverse oscillations. The specific heats calulated from the velocity of sound in the other vapours were in fairly good agreement with those obtained by the spectroscopic method.

In the present paper the results of the measurements of supersonic velocity in the vapours of methylene dichloride, chloroform, carbon tetrachloride and ethylene dichloride, have been reported. The molecular heats deduced from the observed velocity, have been compared with those calculated from the spectroscopic data. The agreement was good in the case of carbon tetrachloride and methylene chloride for which no data are available in literature, but in the case of chloroform, the molecular heats were less by about 3.8 cals. This discordance is similar to that observed previously in the case of *iso*-propyl alcohol. Both of these molecules being of AXB_3 type, it is probable that the rotational specific heats are degraded owing to gyration on A – X axis.

The theory of propagation of sound has undergone remarkable changes during recent years [Herzfeld and Rice (Phys. Rev. 1938, **31,** 691); Kneser (Ann. d. Physik, 1931, **11,** 761 and 777; 1933, **16,** 337); Henry (Nature, 1932, **129,** 200); Zuhlke (Zeits. f. Phys. 1932, **77**, 649); Heil (Ibid. 1932, **74,** 31); Rutgers (Ann. d. Physik, 1933, **16,** 350); Bourgin (Acoust. Soc. J., 1932, **4,** 108; 1933. **5,** 57); Luck (Phys. Rev., 1932, **40,** 440); Richards and Reid (J. Chem. Phys., 1933-34); Teeter (Ibid. 1933, **1,** 251); Rose (Ibid. 1934, **2,** 260)], and it is believed that the results for specific heats obtained by the velocity of sound method, may require reinterpretation in light of a hitherto unsuspected development in the theory of the method. It is claimed that the vibrational heats of most of the gases do not reach equilibrium with the other components of the molecular heat under the conditions of sound velocity determinations, even at audible frequencies.

According to Kneser, the work done in compression in an acoustic cycle is first converted into energy of translation of the molecule parallel to the direction of compression, from where it can be transformed into other translatory degrees of freedom. A part of the energy of translation, is transformed into energy of rotation; from the total stock of energy, a part of the energy of vibration is formed. For every such molecular process there is a definite time of relaxation, and the dispersion region corresponding to the transformation of the energy of translation and rotation, into energy of vibration, may lie at lower frequencies, as the rate of conversion is slow.

The velocity of sound at low frequencies remains at a value V_o, in which the translational, rotational and the vibrational frequencies of the molecule take their full share in the adiabatic cycle. At higher frequencies the velocity may pass through the first dispersive region and remain constant at a value V_1, owing to the time lag between the rotational and transverse vibrational specific heats. When the frequency is further increased, the time period may be too short to permit the transformation of the translational and rotational energy into the energy of all vibrations both transverse and longitudinal, when the velocity will reach a terminal value V_∞. For most of the complex molecules which have been studied in the present series of investigations, the velocity remains constant between 49 and 127 Khz., and corresponds to V_0, the time period being sufficiently slow to allow the equilibrium to be reached between the various degrees of freedom of the molecule. In the case of chloroform, cyclohexane and *tert*-butyl alcohol, the above range of frequency represents probably the V_1 stage, and the increase in absorption and dispersion at the higher frequency was prominently shown. In the case of propyl ether and to a lesser extent *iso*-propyl alcohol, the velocity has apparently reached the V_∞ stage, when only the translational and a part of rotational specific heats, remain active in wave propagation. It is, however, essential to work at both lower and higher frequencies to establish the above speculations.

The failure of a portion of the vibrational degrees of freedom of molecules, which are highly anisotropic, like *n*-hexane and *n*-propyl ether, is in line with the behaviour of molecules like carbon dioxide, carbon disulphide and nitrous oxide. The researches of the author have added molecules of the AXB_3 type to the list of molecules which show absorption and dispersion, which can be attributed to a definite nolecular process.

Owing to the unexpected developments in the theory of propagation of sound it was thought that, molar heats calculated from the velocity at supersonic frequencies, could not be compared with those obtained by the thermal methods and with those calculated from spectroscopic data. Such however is not the case. With minor nteresting and important exceptions (which require further elaboration) he molar heats calculated from the supersonic velocities at 50—127 Khz. are fairly in agreement with those determined by the two other nethods, wherever the data are available.

EXPERIMENTAL.

The apparatus used and the method of measurements have already been described in the previous Parts. As the half wave lengths neasured, were of the order of 1/2 mm, there was always the possibility of miscounting n $\lambda/2$. The results have, therefore, been given in detail Tables 1—10) and have been corrected for the expansion of the reflecor piston by taking the average of the forward and backward readings.

TABLE 1

Methylene chloride 97.1°.

95.82 Khz.						94.16 Khz.	
n	Screw reading mm.	*n*	Screw reading mm.	*n*	Screw reading mm.	*n*	Screw reading mm.
0	1.90	0	5.20	0	4.70	0	134.08
1	3.00	1	6.30	1	5.80	1	132.95
2	4.15	2	7.35	2	6.85	2	131.85
5	7.15	3	8.83	3	7.95	3	130.74
10	12.40	4	9.38	4	8.95	13	119.92
20	24.12	14	20.18	14	19.50	23	109.22
24	27.78	24	30.90	24	30.28	33	98.30
35	39.50	34	41.60	34	41.00	43	87.65
45	50.20	44	52.30	44	51.58	53	76.76
55	61.05	54	62.83	54	62.15	63	66.04
65	71.05	64	73.36	65	73.38	73	55.25
75	82.35	74	84.20	75	84.48	83	44.50
85	93.00	85	96.00	85	95.18	113	12.23
95	103.78	86	97.15	86	96.25	114	11.17
96	104.86	87	98.18	87	97.35	115	10.07
97	105.90	88	99.25	88	98.40	116	8.93
		89	100.35	89	99.50	117	7.75
	95 $\lambda/2$		85 $\lambda/2$		85 $\lambda/2$		114. $\lambda/2$
95—0	101.88	85—0	90.80	85—0	90.48	0—114	122.91
96—1	101.86	86—1	90.85	86—1	90.45	1—115	122.88
97—2	101.55	87—2	90.83	87—2	90.50	2—116	122.92
		88—3	90.92	88—3	90.45	3—117	122.99
		89—4	90.97	89—4	90.55		
	101.76		*90.87*		*90.57*		*122.93*
$\lambda/2$ = 1.070 mm.		$\lambda/2$ = 1.069 mm.		$\lambda/2$ = 1.065mm.		$\lambda/2$ = 1·078 mm.	
mean $\lambda/2$ = 1.068 mm.						Velocity = $n\lambda$ = **203.01 m/sec.**	
Velocity = $n\lambda$ = **204.7 m./sec.**							

TABLE 2

Methylene chloride.

97.1°						134°	
95.82 Khz						93.889 Khz.	
n	Screw reading mm.	*n*	Screw reading mm.	*n*	Screw reading mm.	*n*	Screw reading mm.
0	133 13	0	5 05	0	133.52	0	7 90
1	132.03			1	132.45	3	11.40
2	131.04	2	7.27	2	131.36	4	12 60
3	129.90	3	8.38	3	130.30	5	13.75
25	106.72	26	33.00	23	109.18	25	36.35
46	84.32	46	53.17	43	87.95	45	59.10
66	63.84	66	75 40	63	66.68	65	81.70
85	42.85	86	96.85	93	35.03	85	104 38
115	10 95	117	129.55	113	13.80	105	127 07
118	7 78	118	130 60	118	8.50	107	129 20
119	6.78	119	131 70	119	7.40	108	130.35
120	5.75	120	132.80	120	6 31	109	131 48
121	4.65	121	133.89	121	5 28	110	132 65
	118 $\lambda/2$		118 $\lambda/2$		118 $\lambda/2$		105 $\lambda/2$
0—118	125.35	118—0	125.55	0—118	125.02	108—3	118 95
1—119	125.25	120—2	125 53	1—119	125 05	109—4	118 88
2—120	125.29	121—3	125.51	2—120	125 05	110—5	118 90
3—121	125.25			3—121	125 02		
	125·28		*125·53*		*125 04*		*118·92*
$\lambda/2 = 1{\cdot}062$ mm.		$\lambda/2 = 1{\cdot}064$ mm.		$\lambda/2 = 1{\cdot}059$ mm.		$\lambda/2 = 1{\cdot}133$ mm	
mean $\lambda/2 = 1{\cdot}062$mm.						Velocity $= n\lambda =$ **212.66 m/sec.**	
Velocity $= n\lambda$ $=$ **203.5 m./sec.**							

TABLE 3.

Chloroform 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	$n\ \lambda/2$	Screw reading mm.
0	6.40	0	8.60	0	133·02	0	5·68
1	8.30	1	10.35	1	132·14	1	6·60
2	9.70	4	16.10	2	131·30	3	8·50
3	11·55	5	17.95	3	130·38	4	9·35
13	29·10	15	35.28	4	129·57	5	10·25
33	63·85	35	69.95	24	111·00	26	29·02
43	80.75	45	87.70	54	84·12	46	47·03
53	98.15	55	104.95	64	75·19	66	64·83
63	115.75	65	112,40	84	57·30	86	82·69
69	125,60	69	129.35	104	39·53	106	100·63
70	127.50	70	131·15	124	21·90	126	118·30
71	129,50	71	132·75	134	12·94	136	127·20
72	130,85	72	134·50	138	9·30	138	129·03
73	132,60			140	7,65	140	130·80
				141	6·88	141	131·72
				142	6·07	143	133·53
				143	5·20	144	134·47
	70 $\lambda/2$		66 $\lambda/2$		140 $\lambda/2$		140 $\lambda/2$
70—0	121.10	70—4	115·05	1—141	125·26	140—0	125·12
71—1	121.20	71—5	114·80	2—142	125·23	141—1	125·12
72—2	121·15			3—143	125·18	143—3	125.03
73—2	121.05					144—4	125·12
	121.13		*114.9*		*125 24*		*125·12*
$\lambda/2$ = 1.7304 mm.		$\lambda/2$ = 1.7409 mm.		$\lambda/2$ = 0.8945 mm.		$\lambda/2$ = 0.8937 mm.	
Mean $\lambda/2$=1·7356 mm.				Mean $\lambda/2$ = 0·8941 mm			
Velocity = $n\lambda$ = **171.55 m./sec.**				Velocity = $n\lambda$ = **171·34 m./sec.**			

TABLE 4

Chloroform. 134

Frequency 93 889 Khz.				Frequency 126·264 Khz.	
n	Screw reading mm.	*n*	Screw reading mm.	*n*	Screw reading mm.
0	131.10	0	3 80	0	128.00
1	130.11	1	4·65	1	127 30
2	129.15	3	6 63	2	126.58
3	128.30	4	7 52	3	125.88
4	127.40	5	8.37	4	125 20
14	117.75	6	9 34	5	124·45
24	108.20	7	10.32	15	117·45
34	98 65	8	11 25	25	110.30
44	89.15	48	49 70	35	103.45
54	79.58	58	59.35	56	87.75
64	70·05	68	68.87	66	80.65
74	60.45	78	78 35	67	80.05
84	50.95	88	87.93	68	79 40
94	41.32	98	97 50	69	78·63
104	31.78	108	107.13	70	77.95
114	22.20	118	116 68	73	75 70
124	12.55	128	126 20	75	74.40
125	11·63	129	127.13	76	73.60
126	10.65	130	128.05		
127	9 75	131	129 05		
128	8.85	132	130 05		
	124 $\lambda/2$		124 λ 2		66 λ 2
0—124	118.55	128—4	118 68	0—66	47.35
1—125	118.48	129—5	118.76	1—67	47 25
2—126	118.50	130—6	118 71	2—68	47 18
3—127	118 55	131—7	118.73	3—69	47 25
4—128	118 55	132 -8	118.80	4—70	47 25
	118 53		*118.74*		*47 25*
λ 2=0.9559 mm.		λ 2=0.9575 mm		λ 2=0,7159 mm	
Mean $\lambda/2$=0.9567 mm.				**Velocity** = $n\lambda$ =**180.78 m./sec**	
Velocity= $n\lambda$ =**179.65 m./sec.**					

TABLE 5

Carbon tetrachloride 97.1°.
49.42 Khz.

n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm
0	5·45	0	130·50	0	7·75	0	131·05
1	7·95	1	128·00	1	9·25	1	129·50
2	9·35	11	113·32	2	10·68	2	128·00
22	39·15	22	97·10	22	40·30	22	98·60
42	68·45	42	67·85	42	69·93	41	70·80
62	97·80	62	38·35	62	99·25	61	41·45
72	112·50	72	23·55	72	113·95	71	26·70
82	127·10	82	9·10	82	128·60	82	10·55
83	128·50	83	7·60	83	130·10	83	9·05
84	130·10	84	6·10	84	131·55	84	7·60
85	131·58			85	132·95	85	6·10
	83 λ/2		83 λ/2		83 λ/2		83 λ/2
83—0	122·05	83—0	121·90	83—0	122·35	83—0	122·00
84—1	125·20	84—1	121·90	84—1	122·30	84—1	121·90
85—2	122·23			85—2	122·27	85—2	121·90
	122·16		*121·90*		*122·30*		*121·93*
λ/2 = 1·472 mm.		λ/2 = 1·468 mm.		λ/2 = 1·473 mm		λ/2 = 1·469 mm.	
mean λ/2 = 1·470 mm.				mean λ/2 = 1·471 mm.			
mean λ/2 = 1·4705 mm,							
Velocity = $n\lambda$ = 145.35 m./sec.							

TABLE 6.

Carbon tetrachloride 97.1°.

Frequency 95·82 Khz.				Frequency 126·648 Khz.			
n	Screw reading m m.	*n*	Screw reading mm	*n*	Screw reading mm	*n*	Screw reading mm
0	10·38	0	133·56	0	56·65	0	134·28
1	11·10	1	132·81	2	57·80	1	133·65
2	11·85	2	132·05	3	58·42	2	133·05
		3	131·28	13	64·18	3	132·55
		4	130·49	23	69·90	4	131·98
22	27·00	24	115·30	43	81·30	5	131·40
42	42·26	44	100·18	64	93·35	25	119·94
62	57·48	64	85·10	84	104·77	45	108·47
82	72·67	84	70·00	104	116·22	65	96·98
102	87·77	104	54·82	124	127·70	86	85·00
122	102·81	124	39·60	134	133·37	106	73·55
142	117·94	144	24·45	135	133·97	126	62·10
162	133·13	164	9·28	136	134·49	146	50·60
163	133·88	165	8·48				
164	134·67	166	7·73				
	162 $\lambda/2$		164 $\lambda/2$		132 $\lambda/2$		
162—0	122·75	0—164	124·28	134-2	75·57	Mean of 145 $\lambda/2$	0·5728
163—1	122·78	1—165	124·33	135-3	75·55	,, 144 ,,	·5726
164—2	122·82	2—166	124·32			,, 143 ,,	·5731
						,, 142 ,,	·5731
	122·78		*124·31*		*75·56*		*0·5729*
$\lambda/2=0·7579$ mm.		$\lambda/2=0·7579$ mm.		$\lambda/2=0·5724$ mm.		$\lambda/2=0·5729$ mm,	
mean $\lambda/2=0·7579$ mm.				mean $\lambda/2=0.5726$ mm.			
Velocity $=n\lambda$ **= 145.24 m /sec.**				Velocity $=n\lambda$ **= 145.05 m./sec.**			

TABLE 7

Carbon tetrachloride 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	4·20	0	131·45	0	23·00	0	122·15
1	5·08	1	130·65	1	23·70	1	121·55
2	5·90	2	129·85	3	25·05	2	120·96
3	6·68	4	128·25	4	25·80	3	120·35
4	7·50	14	120·00	5	26·70	23	108·18
5	8·34	24	111·80	6	27·55	43	96·03
35	32·95	34	103·70	25	43·20	63	83·88
45	41·08	44	95·52	35	51·34	83	71·76
55	49·28	54	87·40	45	59·55	118	50·50
65	57·50	64	79·12	65	75·90	128	44·50
85	73·79	84	62·85	85	92·25	138	38·36
104	89·34	104	46·45	105	108·59	139	37·80
124	105·68	124	30·20	125	124·89	140	37·18
144	122·00	144	13·75	126	125·67	141	36·52
154	130·17	145	12·95	127	126·50	142	35·95
155	130·97	146	12·15	128	127·34	143	35·36
156	131·77	147	11·30	129	128·15	144	34·76
157	132·57	148	10·50	130	128·95		
	152 $\lambda/2$		145 $\lambda/2$		125 $\lambda/2$		140 $\lambda/2$
154—2	124-27	0—145	118·50	128—3	102·29	0—140	84·97
155—3	124-29	1—146	118·50	129—4	102·35	1—141	85·03
156—4	124-27	2—147	118·55	130—5	102·25	2—142	85·01
157—5	124·23					3—143	84-99
	124·27		*118·52*		*102·30*		*85·00*
$\lambda/2$ = 0·8176 mm.		$\lambda/2$ = 0·8174 mm		$\lambda/2$ = 0·8184 mm.		$\lambda/2$ = 0·6071 mm.	
mean $\lambda/2$ = 0·8175 mm.				Velocity = $n\lambda$ = **153·6m./sec.**		Velocity $n\lambda$ = **153,6 m./sec.**	
Velocity = $n\lambda$ = **153.5 m./sec.**							

TABLE 8.

Ethylene dichloride 97.1°

Frequency 49.42 Khz.		Frequency 94-16 Khz.			
n	Screw reading mm.	*n*	Screw reading mm.	*n*	Screw reading mm
0	131.40	0	132·56	0	6.18
1	129.60	1	131·62	1	7.15
2	127.65	2	130·67	2	8.05
3	125.75	3	129·68	3	9.05
4	123 05	4	128·76	4	10.00
5	121.50	25	108·55	24	29 32
15	104.15	45	89·35	44	48 53
25	85 80	65	70·12	74	77 38
35	67.60	85	51·00	94	96 58
45	49 15	105	31·70	129	130 15
55	30 70	125	12·46	130	131·10
65	12.40	130	7·55	131	132 05
66	10.50	131	6·70	132	133 00
		132	5·72	134	135 00
	$65\lambda/2$		$130\lambda/2$		$130\ \lambda/2$
65—0	119.00	0—130	125·01	130—0	124 92
66—1	119 10	1—131	124·92	131—1	124 90
		2—132	124·95	132—2	124 95
				134—4	125 00
	119 05		*124·96*		*124.94*
$\lambda/2$ = 1.831 mm		$\lambda/2$ = 0 9612 mm		$\lambda/2$= 0 9612 mm.	
		mean $\lambda/2$ = 0·9612 mm			
Velocity= $n\lambda$ = **180.9 m./sec.**		Velocity= $n\lambda$ = **181.01 m./sec.**			

TABLE 9.

Ethylene dichloride 97.1°

Frequency 95.82 Khz				Frequency 126.648 Khz			
n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm.	n	Screw reading mm
0	111.43	0	5 20	0	37.44	0	133.60
10	101 95	1	6 15	1	38 16	1	132.90
20	92.55	2	7 15	2	38.85	2	132 15
30	83.05	3	8 08	3	39.58	3	131 44
40	73.65	4	9 03	4	40.33	4	130 77
50	64.10	14	18 63	24	54.65	5	130 00
60	54 70	24	28 03	62	81.74	15	122.95
70	45 35	34	37 43	82	96.05	25	115 68
80	35.80	44	46 95	102	110 28	45	101 48
90	26.50	64	65.73	122	124.65	65	87 23
100	17.05	84	84 73	123	125 40	85	72 80
101	16.20	104	103.66	124	126.05	96	65.10
102	15.23	114	113.03	125	126.80	106	57.95
103	14.24	125	123 25	126	127 42	116	50.80
104	13 26	135	132 78	127	128 13	117	50 22
105	12 28	136	133 71	129	129 57	119	48 74
106	11.30	137	136 62	130	130.30	120	48.02
107	10 36	138	135.62	131	131.05	121	47.30
mean of 103 λ/2	0.9436	136—1	135 λ/2 127 56	129—2	127 λ/2 90 72	1—117	116 λ/2 82 68
,, 104 ,,	.9439	137—2	127 47	130—3	90 72	3—119	82 70
,, 105 ,,	.9443	138—3	127 54	131—4	90 72	4—120	82.75
,, 106 ,,	9446					5- 121	82 70
	0·9441		727.52		90·72		82·70
λ/2 = 0.9441 mm.		λ/2 = 0.9446 mm.		λ/2 = 0.7143 mm.		λ/2 = 0 7129 mm.	
mean λ/2 = 0.9443 mm.				mean λ/2 = 0 7136 mm.			
Velocity = $n\lambda$ = **180.95 m./sec.**				Velocity = $n\lambda$ = **180.75 m./sec.**			

TABLE 10

Ethylene dichloride 134°.

93·89 Khz.		126·264 Khz.	
n	Screw reading mm.	*n*	Screw reading mm.
0	18.58	0	128.20
1	19.63	1	127.48
2	20.70	2	126.70
3	21.73	3	129.95
23	42.00	23	110.80
43	62.28	43	94.75
63	82.54	63	80.68
83	102.75	83	65.38
93	112.88	103	50.45
103	123.00	123	35.35
104	124.00	145	18.80
105	125.05	146	18·10
106	126.05	147	17·30
107	127.08	148	16·50
	104 $\lambda/2$		145 $\lambda/2$
104—0	105.42	0—145	109.40
105—1	105.42	1—146	109.38
106—2	105·35	2—147	109.40
107—3	105.35	3—148	109·45
	105.39		*109.41*
$\lambda/2 = 1·0133$ mm.		$\lambda/2 = 0·7545$ mm.	
Velocity = n λ **= 190·27 m·/sec.**		Velocity = n λ **= 190·53 m]sec.**	

TABLE 11.

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
Chloroform	171.5	....	171.3	....	171.4	179.6	180.7	180.2
Methylene chloride	....	203.0	204.1	....	203.5	212.7	....	212.7
Ethylene dichloride	180.9	181.0	180.9	180.8	180.9	190.3	190.5	190.4
Carbon tetrachloride	145.3	....	145.2	145.0	145.2	153.5	153.6	153.6

TABLE 12.

Specific Heats from the Velocity of Sound in Organic Vapours.

	M	p_k	t_k	97.1″						134″					
				V	V^2M/RT	ϕ	γ	C_p-C_v	C_p	V	V^2M/RT	ϕ	γ	C_p-C_v	C_p
Chloroform	119.39	53.8	262.9	**171.4**	1.1384	1.0429	1.1872	2.1598	**13.69**	**179.7**	1.1386	1.0292	1.1718	2.1178	**14.44**
Methylene chloride	84.94	60.9	245.1	**204.0**	1.1485	1,0286	1.1813	2,1248	**13.84**	**212.7**	1.1350	1.0231	1.1612	2.0902	**15.06**
Ethylene dichloride	98,96	50.0	250.0	**180.9**	1,0522	1.0394	1.0936	2.1581	**25.21**	**190.3**	1,0600	1.0291	1.0908	2.1183	**25.44**
Carbon tetra-chloride	153.84	45.0	283.2	**145.2**	1,0544	1.0530	1.1103	2,2153	**22.30**	**153.6**	1.0717	1.0348	1.1090	2,1557	**21.93**

There is no data for the velocity of sound in methylene dichloride reported in literature. From the Tables 1 and 2, the average value for two fractions of the substance, is 204·1 m./sec. at 95 Khz. At 134° measurements were carried out at 94 Khz., at which frequency, the velocity is 212.7 m./sec.

The results for chloroform are given in Tables 3 and 4. There is apparently no dispersion between 50 and 95 Khz. at 97.1°, the mean value of velocity being 171.5 m./sec. At 134° there was a dispersion of nearly 1 meter between 94 and 126 Khz., the measurements at the higher frequencies being difficult owing to absorption. There is only one value reported in the literature for the velocity of sound by Stevens (1900), which is very much lower than the value obtained in the present paper. The other values given in the International Critical Tables have been apparently determined for saturated vapour.

The results for carbon tetrachloride are summarised in Tables 5, 6 and 7. The average velocity at 97.1°, is 145.2 m./ sec., and at 134°, 153.6 m./sec., there being practically no dispersion over the frequency range, at both the temperatures. There are no previous values for the velocity of sound in carbon tetrachloride vapour.

The results for ethylene dichloride are given in Tables 8, 9 and 10. In spite of the complexity of the molecule, there is apparently no dispersion at both the temperatures, over the frequency range studied, the average value of velocity being 180.9 at 97.1° and 190.4 at 134°. There is only one value (176.2 m./sec.) reported in the literature at the boiling point (83.7°) by Billhards Jr. and Bishop Jr. (Jour. Acoust. Soc. Amer. 1936, Vol. **7**, 225-227).

The velocities of sound in vapours at different frequencies are summarised in Table 11. The pressure was 685mm.

Calculation of the Specific Heats from the Velocity of Sound.

The molecular heats have been calculated from the velocity of sound by the usual method. Table 12 gives the results of such calculations.

TABLE 13

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.	△			obs.	cal.	△
Methylene chloride	97.1	13.8	14.2	−0.4	Carbon tetrachloride	0	21.5	21.1	+0.4
	134	15.1	14.8	+0.3		30	20.3	20.7	−0.4
Chloroform	72.5	17.2	17.1	+0.1		70	17.7	21.4	−3.7
	97.1	13.7	17.6	−3.9?		97.1	22.3	21.8	+0.5
	100	16.6	17.6	−1.0		134	21.9	22.2	−0.3
	108.5	17.9	17.7	+0.2					
	134	14.4	18.1	−3.7?					
	175	18.7	18.6	+0.1					

Table 13 shows the comparison of the molecular heats obtained in the present investigation and also those which have been reported, in the literature, with the values obtained by Vold (Jour. Amer. Chem. Soc. 1935, Vol. *57*, 1190—1195) from spectroscopic data. It will be seen that the molecular heats of methylene dichloride, for which there are no data available in literature, are in fair agreement with those calculated from the spectroscopic data.

In the case of chloroform, while most of the results given in the literature are of the same order as those calculated, the results of the present investigation are systemetically less by about 3·8 calories at both the temperatures. As the molelcule is similar to *iso*-propyl alcohol the spin on the C—H axis will result in loss of R calories for the other two degrees of rotation, the balance (1.8) may be due to partial loss by C—Cl transverse linkage, but not to a dispersive region. This fact taken along with the higher absorption observed in this vapour, shows that the velocity has already suffered one transition below 50 Khz. and that the second dispersive region has already been felt at 127 Khz.

The results indicate that there is a dropping out from the acoustic cycle, a group of rotational and concomitant vibrational states. The apparent reason for the suppression of the rotational degree of freedom which contributes R calories in the case of *iso*-propyl alcohol, and $\frac{1}{2}$R calorie in the case of *tert*-butyl alcohol, is the degradation of the rotational energy into that of gyration owing to quasi-tetrahedral structure AXB_3 of these molecules.

In the case of carbon tetrachloride, although it comes under the same category as *tert*-butyl alcohol, the results at 97.1° and 134° are in fair agreement with those calculated, and also with those given in literature, which indicates that all the heat capacity remains fully active in the range of frequencies studied. It is interesting to note, however, that one of the values reported in literature at 70° is 3.7 calories less than that calculated from the spectroscopic data just as in the case of the results with chloroform, found in the present investigation. The degradation observed in the case of *tert*-butyl alcohol may be due to unequal loading of the tertiary carbon atom.

It has been shown that there is a concomitant dropping out of rotational and deformational vibrational degrees of freedom in a comparatively low frequency range. The reason for the suppression of some of the rotational states in the molecules of the AXB_3 type, is the gyration of the molecule along the A—X axis on account of the high moment of inertia of the molecule. Such a gyration of the molecule may have resonance frequencies below 50 Khz. The suppression of the bending oscillations from taking part in the specific heats also readily follows, on the basis of the gyration of the molecule.

Unfortunately the frequencies of this order (50—100 Khz.) are too small to be observed by any spectroscopic method. A study of the rotational lines in the far ***infra red*** shows spacings of the order of 1 cm^{-1} for molecules like CH_3Cl, which may be smaller for heavy molecules like $CHCl_3$. In the case of such molecules it may not be possible to resolve the fine structure lines, although information regarding the moment of inertia may be obtained from the nature of the "envelop" and by actual calculation from molecular data.

In the case of the molecules which are increasingly anisotropic like *n*-hexane and *n*-propyl ether, it is suggested that, there is a partial loss of the specific heat due to rotational energy and deformational energy. This effect is more pronounced longer the chain, because at 50 Khz., methyl ether shows normal specific heat, while ethyl ether indicates a slight diminution, and propyl ether has reached the complete transition to V_∞ stage. The probable manner by which such molecules can show the phenomena of absorption and dispersion, is by orientation of the molecule with its length in the direction of propagation of sound. Such an arrangement can convert the translational energy of the molecule into the vibrational energy, by the end on collision, and will result in a loss of one rotational state out of the two, which are possible for linear molecules.

Although further work is essential to establish the above speculations, the possibility of multiple transitions in supersonic velocity which was originally put forth by W. T. Richards, has been partially substantiated by the results of the author, and does not now appear to be entirely fantastic.

The results of the investigations presented in Parts I—VII of this series clearly indicate the desirability of an intensive programme of work in this fascinating field. It is necessary to reach the accuracy of the optical interferometer by paying special attention to the various physical factors and to extend the measurements to both higher and lower frequencies at higher temperatures, where the corrections for the compressibility introduce less uncertainties. Several difficulties in the work have now been overcome, and further work on these lines is in progress.

SUMMARY.

The supersonic velocities in vapours of dichloromethane, chloroform, carbon tetrachloride and ethylene dichloride have been measured at 97.1° and 134°, over a range of 50—127 Khz. It has been found that

in the case of chloroform, there is an appreciable dispersion at the higher frequency.

The molecular heats of the various vapours, calculated from the measured velocities, are in fair agreement with those calculated from the spectroscopic data, except in the case of chloroform, which shows a diminution of the molecular heat by about 3.8 cals. at both the temperatures owing to a definite transition in supersonic velocity.

It has been pointed out that most of the molecules which have shown either dispersion or transition in the velocity of sound over the frequency range studied, are of AXB_3 type, or are highly anisotropic.

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.
Chloroform	171.4	1.1872	13.7	17.6	179.7	1.1718	14.4	18.1
Methylene chloride	204.0	1.1813	13.8	14.2	212.7	1.1612	15.1	14.8
Ethylene dichloride	180.9	1.0936	25.2	—	190.4	1.0908	25.4	—
Carbon tetrachloride	145.2	1.0886	22.3	21.8	153.6	1.1090	21.9	22.2

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