LXX.—*The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Heptane.*

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IN previous papers (Trans., 1897, **71**, 446; 1895, **67**, 1071), the vapour pressures, specific volumes, and critical constants of normal pentane and normal hexane have been given, and it has been pointed out that, whilst the generalisations of Van der Waals regarding "corresponding" pressures, temperatures, and volumes hold good for these substances with a near approach to accuracy, yet the small deviations appear to depend on the molecular weight. Naturally, however, it would be unsafe to generalise from experiments with only two members of a series, and the hope was expressed that it would be possible to obtain data for normal heptane and normal octane.

Dr. Thorpe has very kindly placed his well-known specimen of normal heptane from *Pinus sabiniana* at my disposal, and I am now able to give the data for this paraffin. It will be seen that they are in agreement with the conclusions previously arrived at.

The boiling point of normal heptane is 98·43°, and the sp. gr. at 0° is 0·70048 (Thorpe, Trans., 1880, **37**, 213).

Vapour Pressures at Low Temperatures.

The method of Ramsay and Young was employed for pressures up to 160 mm.; for higher pressures up to that of the atmosphere a modified distillation bulb with reflux condenser was used.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
9·2	−3·4°	46·05	25·05°	153·8	51·95°	382·1	76·5°
10·6	−1·1	57·35	29·65	186·2	56·85	431·2	80·2
12·45	+1·2	71·45	34·35	205·2	59·4	485·5	83·8
15·3	5·0	91·0	40·15	229·6	62·35	547·2	87·45
18·15	8·05	112·4	44·95	257·7	65·55	610·7	91·15
22·65	11·7	136·4	49·4	294·3	69·2	687·8	95·15
28·95	16·1	151·7	51·4	334·4	72·65	762·35	98·55
36·15	20·35						

The vapour pressures at high temperatures were determined with the pressure apparatus employed in previous researches, and the usual corrections were made.

The observed pressures (the mean of four readings in each case) together with those read from the curves constructed from the observations at low temperatures, and also the pressures calculated by means of Biot's formula

$$\log p = a + b\ \alpha^t + c\ \beta^t$$

are as follows.

The constants for Biot's formula are—

$$a = 1{\cdot}145148$$

$$b = 2{\cdot}431040 \qquad \log b = 0{\cdot}3857922$$

$$c = -2{\cdot}517688 \qquad \log c = 0{\cdot}4010018$$

$$\log \alpha = 0{\cdot}00053408$$

$$\log \beta = \bar{1}{\cdot}99596377$$

$$t = t^\circ C.$$

Vapour Pressures.

Temperature.	Dynamical method from curve.	Statical method.	Calculated from Biot's formula.	Temperature.	Statical method.	Calculated from Biot's formula.
0°	11·45	—	11·45	150°	2784	2780·4
10	20·50	—	20·51	160	3450	2433·3
20	35·50	—	35·16	170	4212	4196·0
30	58·35	—	57·87	180	5091	5080·9
40	92·05	—	91·78	190	6095	6101·3
50	140·9	—	140·74	200	7261	7271·8
60	208·9	—	209·32	210	8594	8608·6
70	302·3	—	302·77	220	10105	10130
80	426·6	—	407·26	230	11810	11857
90	588·8	—	588·74	240	13790	13811
100	795·2	—	794·93	250	15980	16020
110	—	1047	1053·3	260	18470	18511
120	—	1367	1372·1	264	19610	19595
130	—	1753	1759·9	266·85	20430	20399
140	—	2229	2226·1	(Crit.)		

The critical temperature was taken to be 266·9°, and the critical pressure 20415 mm.

Volumes of a Gram of Liquid.

These were determined in the pressure apparatus: up to 210° the volumes were read directly, but at higher temperatures they were calculated from observations of the volume of vapour, and the total volume of liquid and vapour by the method described in the Transactions (1893, **63**, 1200).

The observed and smoothed specific volumes and the molecular volumes calculated from the smoothed specific volumes are given in the following table. From 0° to 100°, the smoothed values have been calculated from Thorpe's table of volumes of normal heptane—$V_0 = 1{\cdot}00000$—(*loc. cit.*).

The molecular weight is taken as 99·79.

Volumes of a Gram and Molecular Volumes of Liquid.

Temperature.	Volumes of a gram.		Molecular volumes	Temperature.	Volumes of a gram.		Molecular volumes
	Observed.	From curve.			Observed.	From curve.	
0°	—	1·4276	142·46	170°	1·8669	1·8660	186·21
10	—	1·4450	144·20	180	1·9126	1·9112	190·72
20	—	1·4629	145·98	190	1·9625	1·9620	195·79
30	1·4804	1·4813	147·82	200	2·0192	2·0195	201·53
40	1·5000	1·5003	149·72	210	2·0867	2·0865	208·21
50	1·5204	1·5200	151·68	220	2·1670	2·1665	216·20
60	1·5417	1·5406	153·74	230	2·2650	2·2655	226·07
70	1·5613	1·5621	155·88	240	2·3940	2·3940	238·90
80	1·5856	1·5846	158·13	250	2·5730	2·5730	256·80
90	1·6081	1·6082	160·48	256	2·7290	2·7290	272·30
100	1·6327	1·6330	162·96	260	2·8950	2·8930	288·70
110	1·6591	1·6591	165·56	262	3·0010	3·0010	299·50
120	1·6888	1·6875	168·40	264	3·1590	3·1590	315·20
130	1·7176	1·7180	171·44	265	3·2690	3·2690	326·20
140	1·7516	1·7510	174·74	266	3·4400	3·4400	343·30
150	1·7863	1·7862	178·25	266·5	3·5480	3·5480	354·10
160	1·8236	1·8245	182·07	266·9 (Crit.)	—	4·266*	425·7*

* By the method of Cailletet and Mathias.

Volumes of a Gram of Saturated Vapour.

Determinations were made with the pressure apparatus and by the sealed tube method (Trans., 1891, **59**, 37, and *Phil. Mag.*, 1895).

The results are given in the table below, also the volumes of a gram read from curves constructed by plotting the logarithms of the volumes against the temperatures. The molecular volumes calculated from the smoothed specific volumes are also given.

Volumes of a Gram and Molecular Volumes of Saturated Vapour.

Temperature.	Volumes of a gram. Pressure apparatus.	Sealed tube method. I.	Sealed tube method. II.	From curves.	Molecular volumes.
70°	—	—	697	697	69500
80	—	—	516	501	50000
90	—	—	381	370	36900
100	—	—	280	279	27800
110	—	—	212	213·1	21250
120	—	—	165	164·8	16450
130	—	—	128·8	129·0	12870
140	—	—	102·5	102·3	10210
150	—	—	81·8	81·8	8170
160	—	—	66·2	66·3	6620
170	—	54·8	53·9	54·1	5400
180	—	45·3	44·15	44·6	4450
190	—	36·9	—	36·8	3675
200	—	30·3	—	30·27	3020
210	—	25·0	—	24·97	2492
220	20·44	20·45	—	20·44	2040
230	16·66	16·66	—	16·66	1663
240	13·45	13·40	—	13·43	1340
250	10·60	10·53	—	10·57	1055
256	8·97	8·91	—	8·95	894
260	7·77	7·77	—	7·77	776
262	7·18	7·165	—	7·16	715
264	6·50	6·480	—	6·50	649
265	6·10	—	—	6·13	612
266	5·60	5·645	—	5·625	561
266·5	5·28	—	—	5·280	527
266·9 (Crit.)	—	—	—	4·266*	425·7*

* By the method of Cailletet and Mathias.

The critical volume of a gram and molecular volume were calculated from the critical density, which was ascertained by the method of Cailletet and Mathias (*Compt. rend.*, 1886, **102**, 1202; 1887, **104**, 1563; 1892, **115**, 35).

The densities of liquid and saturated vapour, the mean densities and those calculated from the formula

$$D_t = 0{\cdot}3518 - 0{\cdot}00044t$$

are given below.

Temperature.	Density.		Mean density.		
	Liquid.	Saturated vapour.	Observed.	Calculated.	$\Delta \times 10^4$
70°	0·6402	0·0014	0·3208	0·3210	−2
80	0·6311	0·0020	0·3165	0·3166	−1
90	0·6218	0·0027	0·3122	0·3122	0
100	0·6124	0·0036	0·3080	0·3078	+2
110	0·6027	0·0047	0·3037	0·3034	+3
120	0·5926	0·0061	0·2993	0·2990	+3
130	0·5821	0·0078	0·2949	0·2946	+3
140	0·5711	0·0098	0·2904	0·2902	+2
150	0·5598	0·0122	0·2860	0·2858	+2
160	0·5481	0·0151	0·2816	0·2814	+2
170	0·5359	0·0185	0·2772	0·2770	+2
180	0·5232	0·0224	0·2728	0·2726	+2
190	0·5096	0·0272	0·2684	0·2682	+2
200	0·4952	0·0330	0·2641	0·2638	+3
210	0·4793	0·0401	0·2597	0·2594	+3
220	0·4616	0·0489	0·2552	0·2550	+2
230	0·4414	0·0600	0·2507	0·2506	+1
240	0·4177	0·0745	0·2461	0·2462	−1
250	0·3877	0·0946	0·2416	0·2418	−2
256	0·3664	0·1117	0·2390	0·2392	−2
260	0·3457	0·1287	0·2372	0·2374	−2
262	0·3332	0·1396	0·2364	0·2365	−1
264	0·3166	0·1538	0·2352	0·2356	−4
265	0·3059	0·1631	0·2345	0·2352	−7
266	0·2907	0·1778	0·2342	0·2348	−6
266·5	0·2819	0·1895	0·2357	0·2345	+12
266·9	—	—	—	0·2344	—

The critical constants are thus found to be—

Temperature 266·9°.
Pressure 20415 mm.
Density 0·2344. Volume of a gram 4·266 c.c.
Molecular volume 425·7.

It is noticeable that the critical densities of the four paraffins so far investigated are nearly identical; they are

Isopentane	0·2344
Normal pentane	0·2324
Normal hexane	0·2343
Normal heptane	0·2344

The absolute temperatures and the molecular volumes of liquid and saturated vapour were read from the curves at a series of pressures "corresponding" with those given in previous papers: from these data the ratios of the temperatures and volumes to the critical constants were calculated, also the ratios of the actual to the theoritical densities of saturated vapour.

Ratio of pressure to critical pressure.	Pressure.	Absolute tempera-ture.	Molecular volume.		$\frac{\text{Abs. temp.}}{\text{Abs. crit. temp.}}$	$\frac{\text{Vol. liq.}}{\text{Crit. vol.}}$	$\frac{\text{Vol. sat. vap.}}{\text{Crit. vol.}}$	$\frac{\text{Density sat. vap.}}{\text{Theor. density.}}$
			Liquid.	Saturated vapour.				
0·001474	30·1	290·0°	145·44	—	0·5371°	0·3416	—	—
0·002949	60·2	303·7	147·94	—	0·5625	0·3475	—	—
0·005898	120·4	319·2	150·94	—	0·5912	0·3545	—	—
0·011795	240·8	336·75	154·58	—	0·6237	0·3631	—	—
0·022411	457·5	355·2	158·68	46700	0·6579	0·3727	109·6	1·033
0·044232	903·0	377·25	164·02	24780	0·6987	0·3853	58·2	1·048
0·088465	1806	404·0	171·78	12580	0·7483	0·4035	29·5	1·105
0·14744	3010	426·75	179·62	7570	0·7904	0·4219	17·8	1·164
0·20642	4214	443·0	186·21	5403	0·8205	0·4374	12·7	1·209
0·29488	6020	462·15	195·29	3729	0·8560	0·4587	8·76	1·279
0·44232	9030	485·85	210·36	2353	0·8999	0·4941	5·53	1·421
0·58978	12040	504·0	227·17	1626	0·9335	0·5336	3·82	1·600
0·73721	15050	518·75	248·18	1172	0·9608	0·5830	2·75	1·827
0·82568	16860	526·5	265·25	964	0·9752	0·6230	2·26	2·013
0·88465	18060	531·3	280·91	827	0·9841	0·6598	1·95	2·210
0·94363	19260	535·75	304·76	691	0·9923	0·7159	1·62	2·500
0·97313	19870	537·95	325·51	614	0·9964	0·7646	1·44	2·741
1·00000	20415	539·9	425·7	425·7	1·0000	1·0000	1·00	3·860

The influence of the molecular weight of the normal paraffins will be fully discussed when the data for normal octane have been obtained; meanwhile, it may be pointed out that, as with the ethereal salts, the ratios of the absolute temperatures (boiling points) at corresponding pressures to the absolute critical temperatures show a small but decided increase with rise of molecular weight. No definite relation between the volume ratios and the molecular weights of the ethereal salts could be traced, but in the case of the three normal paraffins so far studied, it appears that the ratios of the volumes of saturated vapour to the critical volumes, and of the actual to the theoretical critical densities, also increase with rise of molecular weight, whilst the ratios of the volume of liquid to the critical volume diminish slightly.

In the table below are given the ratios of the actual to the theoretical densities at the critical points and the other ratios at a single "reduced" pressure.

	Normal pentane.	Normal hexane.	Normal heptane.
$\frac{\text{Actual critical density.}}{\text{Theoretical critical density.}}$	3·765	3·827	3·860

Ratio of Pressure to Critical Pressure = 0·14744.

$\frac{\text{Absolute temperature.}}{\text{Absolute critical temperature.}}$	0·7769	0·7831	0·7904
$\frac{\text{Volume of liquid.}}{\text{Critical volume.}}$	0·4245	0·4234	0·4219
$\frac{\text{Volume of saturated vapour.}}{\text{Critical volume.}}$	17·0	17·6	17·8