

LXXXIII.—*The Vapour Pressures, Specific Volumes and Critical Constants of Hexamethylene.*

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A SMALL quantity of hexamethylene was obtained by one of us (Trans., 1898, 73, 932) by the long-continued fractional distillation of Galician petroleum. The liquid boiled quite constantly at  $80\cdot8^{\circ}$ ; its specific gravity at  $0^{\circ}/4^{\circ}$ ,  $0\cdot7903$ , agreed perfectly with that of a specimen prepared synthetically by Markownikoff (*Annalen*, 1898, 302, 1), and the results obtained on analysis were quite satisfactory. The fraction with the constant boiling point was also the one that possessed the highest specific gravity. For these reasons, the specimen was regarded as pure. When the vapour pressures of the hexamethylene at low temperatures were being determined by the method of Ramsay and Young, it was noticed that partial solidification took place in the condenser, which was cooled by a freezing mixture. It thus became evident that the substance had a higher freezing point than had previously been supposed. It was found, however, to be far from constant—say  $-12^{\circ}$  to  $-7^{\circ}$ —depending on the relative quantities of solid and liquid.

It is clear, then, that hexamethylene from petroleum contains a certain amount of a hydrocarbon, probably a heptane such as trimethylpropylmethane, boiling at a temperature near to  $81^{\circ}$ , and inseparable from the hexamethylene by fractional distillation.

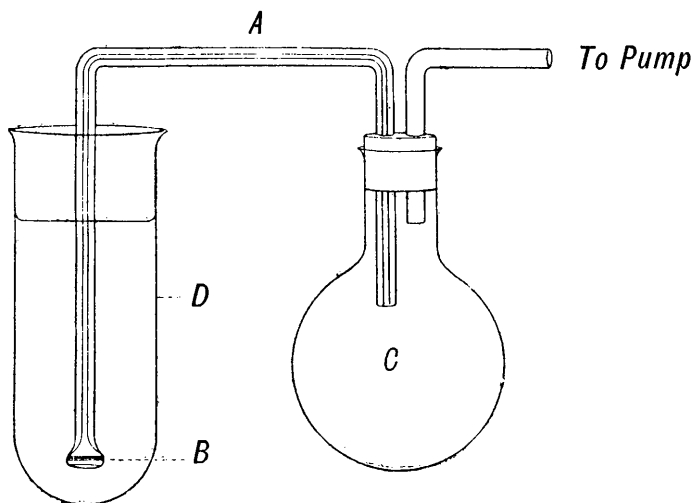
It seemed probable that the impurity might be removed by fractional crystallisation, but as the amount of material was very small, we thought it advisable to utilise, if possible, the less pure fraction ( $76-78\cdot5^{\circ}$ ) left over after the chemical investigation of hexamethylene had been completed (Trans., 1898, 73, 932).

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This liquid was first redistilled with a 12 column Young and Thomas dephlegmator, when the greater portion came over between  $77.5^{\circ}$  and  $80^{\circ}$ . A partial purification of this fraction was effected by treatment with chlorosulphonic acid (Trans., 1899, 75, 172), both the boiling point and specific gravity being thereby raised, whilst the freezing point became sufficiently high to admit of partial solidification in a mixture of solid carbon dioxide and ether.

The separation of the crystals from the mother liquor was effected by means of the apparatus shown in Fig. 1. A piece of thick-walled

FIG. 1.

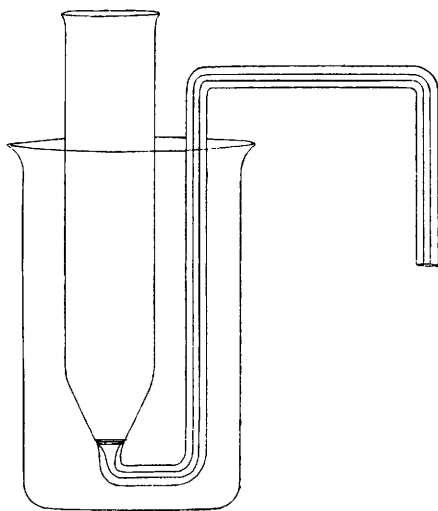


tubing, A, of about  $1\frac{1}{2}$  mm. bore was bent twice at right angles; one end, B, was enlarged into a small funnel into which were fused three circular pieces of platinum gauze as nearly as possible in contact with each other. The other limb of the tube was connected with a round bottomed flask, C, which could be exhausted. The liquid was first partially frozen in the open tube, D, and the tube A was then placed in position as shown in the diagram, and the pump set in action. The meshes of the gauze effectually prevented the passage of the crystals, although they were exceedingly small, and the residue appeared hard and snowy, notwithstanding that, owing to its porous nature, it still retained a considerable amount of liquid impurity. The residue, after fusion, was partially solidified by means of a freezing mixture containing more ether, and this operation was continued until the freezing point of the hexamethylene had risen above  $-40^{\circ}$ , when a second apparatus (Fig. 2) was employed.

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This apparatus consisted of a wide, cylindrical tube drawn out below and fused to a thick-walled tube of narrow bore, bent four times at right angles. Three pieces of platinum gauze were fused into the wide tube just above the junction with the narrow one. Mercury was poured into the vessel until it rose well above the platinum gauze, and the narrow tube was connected with a round-bottomed flask, which, as before, was attached to a pump. The liquid to be frozen was then placed in the wide tube, and was cooled by a suitable freezing mixture, such a temperature being always chosen that only partial solidification could take place. After the solidification had reached its limit, the bulb was exhausted, when the mercury, followed by the mother liquor, was carried over into it, the residue meanwhile being well pressed

FIG. 2.



down. This apparatus is more effective than the first, but can obviously only be used for temperatures above the freezing point of mercury. By a series of fractional crystallisations carried out as described, a quantity of hexamethylene was obtained equal in purity to the best specimen; the fractions were then mixed together, and the further purification proceeded with.

After a few more recrystallisations, ice could be used as the freezing agent, and the melting point finally rose to  $4.7^{\circ}$ . Although there was still a slight fall of temperature before solidification was complete, this may be taken as very close indeed to the true melting point of hexamethylene, and our specimen may be regarded as so pure that the errors in the physical constants would be inappreciable.

*Specific Gravity.*

Owing to the readiness with which hexamethylene solidified at  $0^{\circ}$ , it was not possible to make a direct determination of the specific gravity at this temperature, but the constant was calculated from the volume of a gram read from a curve constructed from the observations at higher temperatures. The specific gravities were directly determined with a Sprengel tube, as modified by Perkin, at  $10.7^{\circ}$  and  $14.5^{\circ}$ ; the weighings were in all cases reduced to a vacuum.

Temperature.	Specific gravity
$0^{\circ}$	0.79675
$10.7$	0.78715
$14.5$	0.78280

*Specific gravities by other observers.*

Name.	Reference.	Sp. gr. at $t^{\circ}$ .	Calc. at $0^{\circ}/4^{\circ}$ .*
Brühl † .....	<i>Ber.</i> , 1894, <b>27</b> , 1065.	0.790 at $20^{\circ}/4^{\circ}$	0.8090
Markownikoff ‡ .....	<i>Ann.</i> , 1898, <b>302</b> , 1.	0.7902 at $0^{\circ}/6^{\circ}$	0.7901
		0.7727 at $20^{\circ}/0^{\circ}$	0.7912
Zelinsky ‡ .....	<i>Ber.</i> , 1895, <b>28</b> , 1022.	0.7764 at $20^{\circ}/4^{\circ}$	0.7951

\* Assuming the expansion from  $0^{\circ}$  to  $20^{\circ}$  to be the same as for our specimen.

† Prepared synthetically by Baeyer (*Annalen*, 1893, **278**, 88).

‡ Prepared synthetically.

Our value agrees best with that of Zelinsky; the specimen used by Brühl must have contained some heavy impurity.

*Boiling point.*

Press.	Temp.	Corr. to 760 mm.
754.7	$80.65^{\circ}$	$80.9^{\circ}$
759.75	$80.8$	$80.8$
Mean		80.85

Calculated from the constants for Biot's formula, the boiling point is  $80.9^{\circ}$ , and the value of  $dp/dt$  at the boiling point = 22.75 mm. per degree.

*Boiling points by other observers.*

Name.	Boiling point.	Reduced to 760 mm.
Baeyer .....		79 —79·5°
Markownikoff		80·5—81
Zelinsky .....	81—82° at 740 mm.	about 82 —83

Markownikoff's boiling point agrees well with ours, but Baeyer's is decidedly too low and Zelinsky's too high.

*Vapour Pressures at Low Temperatures.*

For pressures up to 270 mm., the method of Ramsay and Young was employed; from 153 mm. to the atmospheric pressure, a modified distillation bulb with reflux condenser was used.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
19·95	- 5·35°	42·45	7·95°	101·65	26·2°	217·9	44·5°
20·95	- 4·50	49·9	11·2	115·35	29·05	243·1	47·3
23·05	- 3·05	58·0	14·25	132·4	32·25	272·3	50·45
26·7	- 0·50	68·05	17·5	153·05	35·65		
31·2	+ 2·20	78·25	20·7	173·1	38·65		
36·35	5·05	89·45	23·25	194·7	41·45		
153·5	35·55	242·4	47·25	373·4	59·0	559·5	71·0
173·1	38·45	271·0	50·15	409·6	61·7	617·3	74·1
193·4	41·25	301·5	53·1	462·1	65·3	670·4	76·75
217·1	44·35	336·5	56·15	511·7	68·35	713·9	78·8

The vapour pressures at high temperatures were determined with the pressure apparatus employed by one of us 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,

$$\log p = a + bt + ct^2$$

are given in the following table.

The constants for Biot's formula are :

$$\begin{aligned} a &= 1·424527 \\ b &= 2·354051 & \log b &= 0·3718160 \\ c &= -2·333778 & \log c &= 0·3680596 \\ \log a &= 0·00049715 \\ \log \beta &= 1·99608748 \\ t &= t^{\circ}\text{C} \end{aligned}$$

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*Vapour pressures.*

Temperature.	Dynamical method from curve.	Statistical method.	Calculated from Biot's formula.	Temperature.	Statistical method.	Calculated from Biot's formula.
0°	27·55		27·85	150°	4123	4124·5
10	47·05		47·09	160	5028	5007·3
20	76·9		76·58	170	6041	6021·9
30	121·35		120·16	180	7194	7199·9
40	181·65		182·49	190	8482	8494·5
50	269·2		269·05	200	9977	9980·2
60	385·0		386·07	210	11651	11651
70	540·8		540·51	220	13511	13526
80	741·3		739·91	230	15601	15622
90		992	992·34	240	17973	17961
100		1304	1306·8	250	20529	20565
110		1687	1691·0	260	23439	23461
120		2152	2155·4	270	26667	26680
130		2703	2709·1	277	29206	—
140		3362	3362·0	279·95 (Critical)	30260	30234

The critical temperature was taken to be 280·0° and the critical pressure 30252 mm.

*Volumes of a Gram of Liquid.*

These were determined in the pressure apparatus; up to 180°, the volumes were read directly, but at higher temperatures they were

*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°	—	1·2551	105·20	170°	1·6131	1·6130	135·20
10	—	1·2700	106·45	180	1·6481	1·6482	138·15
20	—	1·2855	107·75	190	1·6910	1·6875	141·45
30	1·3018	1·3012	109·07	200	1·7300	1·7302	145·03
40	1·3170	1·3174	110·43	210	1·7805	1·7775	148·99
50	1·3346	1·3341	111·83	220	1·8300	1·8327	153·62
60	1·3513	1·3514	113·27	230	1·8975	1·8970	159·01
70	1·3689	1·3688	114·73	240	1·9745	1·9750	165·55
80	1·3873	1·3878	116·33	250	2·0745	2·0745	173·90
90	1·4064	1·4073	117·96	260	2·2083	2·2060	184·9
100	1·4279	1·4279	119·69	265	2·2940	2·297	192·5
110	1·4503	1·4496	121·51	270	2·4240	2·424	203·2
120	1·4734	1·4726	123·43	274	2·5670	2·570	215·4
130	1·4970	1·4970	125·51	277	2·7470	2·746	230·2
140	1·5232	1·5233	127·69	279	2·9470	2·947	247·0
150	1·5507	1·5509	130·00	280	—	3·659*	306·7*
160	1·5811	1·5810	132·52				

\* By the method of Cailletet and Mathias.

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calculated from observations of the volume of vapour and the total volume of liquid and vapour by the method described by one of us 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 foregoing table.

The molecular weight is taken as 83·82.

## *Volumes of a Gram of Saturated Vapour.*

Determinations were made with the pressure apparatus and by the sealed tube method (Trans., 1891, 59, 37; *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.				Molecular volumes.
	Pressure apparatus.	Sealed tube method.		From curves.	
		I.	II.		
90°		267		266	22300
100		203		204	17100
110		159		159	13300
120		125·5		125·5	10530
130		100·4		100·0	8380
140		80·9		80·8	6775
150		66·4		66·3	5560
160		54·6	54·6	55·0	4610
170			46·0	45·8	3840
180			38·4	38·1	3190
190	31·1		31·7	31·85	2670
200	26·9		26·8	26·75	2243
210	22·3		22·6	22·54	1890
220	19·20		19·0	19·05	1597
230	16·02		16·0	16·00	1341
240	13·38		13·32	13·34	1118
250	11·06		11·02	11·04	926
260	8·99		8·95	9·00	754
265	8·05		7·97	8·01	671
270	6·96		6·97	6·98	585
274	6·14		6·10	6·12	513
277	5·39		—	5·39	452
279	4·75		—	4·75	398
280	—		—	3·659*	306·7*
(Critical)					

\* By the method of Cailliet and Mathias.

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The critical volume of a gram and the 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  $D_t = 0.3954 - 0.000436t$  are given below.

Temperature.	Densities.		Mean densities.		
	Liquid.	Saturated vapour.	Observed.	Calculated.	$\Delta \times 10^4$ .
90°	0.7106	0.0038	0.3572	0.3562	- 10
100	0.7003	0.0049	0.3526	0.3518	-- 8
110	0.6898	0.0063	0.3481	0.3474	- 7
120	0.6791	0.0080	0.3435	0.3431	- 4
130	0.6680	0.0100	0.3390	0.3487	- 3
140	0.6566	0.0124	0.3344	0.3344	0
150	0.6448	0.0151	0.3299	0.3300	+ 1
160	0.6325	0.0182	0.3254	0.3256	+ 2
170	0.6200	0.0218	0.3209	0.3213	+ 4
180	0.6067	0.0262	0.3165	0.3169	+ 4
190	0.5926	0.0314	0.3120	0.3126	+ 6
200	0.5780	0.0374	0.3077	0.3082	+ 5
210	0.5626	0.0444	0.3035	0.3038	+ 3
220	0.5456	0.0525	0.2991	0.2995	+ 4
230	0.5271	0.0625	0.2948	0.2951	+ 3
240	0.5063	0.0750	0.2907	0.2908	+ 1
250	0.4820	0.0906	0.2863	0.2864	+ 1
260	0.4533	0.1112	0.2822	0.2820	- 2
265	0.4354	0.1249	0.2801	0.2799	- 2
270	0.4125	0.1432	0.2779	0.2777	- 2
274	0.3891	0.1633	0.2762	0.2759	- 3
277	0.3642	0.1857	0.2749	0.2746	- 3
279	0.3393	0.2105	0.2749	0.2738	- 11
280	—	—	—	0.2733	
(Critical)					

It may be interesting to compare the critical and other constants of the hydrocarbons, benzene, hexamethylene, and normal hexane, as they all contain six atoms of carbon in the molecule, but differ essentially in constitution. The data are given in the following table :

	Benzene.	Hexamethylene.	N. Hexane.
Melting point .....	5.6°	4.7°	?
Boiling point (760 mm.) ....	80.2°	80.9°	68.95°
Specific gravity 0°/4° .....	0.90000	0.79675	0.67697
Critical temperature .....	288.5°	280.0°	234.8°
Critical pressure in mm. ....	36395	30252	22510
Critical density .....	0.3037	0.2733	0.2343
Critical volume of a gram ...	3.293	3.659	4.268
Critical molecular volume ...	256.3	306.7	366.3



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In its behaviour with chemical reagents, hexamethylene shows a much closer resemblance to normal hexane than to benzene, but, on the other hand, in certain of its physical properties it exhibits a most striking relationship to benzene; thus their melting points and boiling points differ respectively by less than a degree, whilst the critical temperature of hexamethylene is only  $8.5^{\circ}$  lower than that of benzene, but is  $45.2^{\circ}$  higher than that of normal hexane. The specific gravity at  $0^{\circ}$ , the critical density, and the critical pressure of hexamethylene lie, however, about midway between those of the other two hydrocarbons.

The absolute temperatures and the molecular volumes of liquid and saturated vapour were read from the curves at a series of pressures "corresponding" to 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 theoretical densities of saturated vapour.

For the sake of comparison, the ratios for benzene and normal hexane, the other two six-carbon hydrocarbons so far investigated, are given in addition to those of hexamethylene in the following tables:

Ratios to critical pressures.	Pressures.	Absolute temperatures.	Molecular volumes.		Ratios of actual to theoretical densities of saturated vapour.		
			Liquid.	Saturated vapour.	Hexamethylene.	Benzene.	Normal hexane.
0.001474	44.60	281.85°	106.30				
0.002949	89.21	296.05	108.14				
0.005898	178.4	312.25	110.32				
0.011795	356.8	330.95	112.97				
0.022411	678.0	350.05	115.85				
0.044232	1338	373.8	119.82	16800	1.033	1.052	1.069
0.088465	2676	402.45	125.37	8490	1.101	1.091	1.103
0.14744	4460	426.6	130.89	5200	1.143	1.136	1.153
0.20642	6245	444.65	135.68	3720	1.189	1.180	1.218
0.29488	8921	466.1	142.54	2530	1.282	1.260	1.302
0.44232	13380	492.25	153.27	1620	1.411	1.408	1.445
0.58978	17840	512.5	165.17	1128	1.582	1.582	1.621
0.73721	22300	529.0	180.13	822	1.793	1.806	1.851
0.82568	24980	537.55	191.74	680	1.967	2.006	2.034
0.88465	26760	543.0	203.18	585	2.154	2.180	2.219
0.94363	28545	548.25	220.87	486	2.454	—	2.517
0.97313	29440	550.8	235.96	432	2.689	—	2.774
1.00000	30252	553.0	306.7	306.7	3.703	3.741*	3.827

\* By an error in copying, this number has been given as 3.710 in previous papers.

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Ratios to critical pressures.	Absolute Temperature. Absolute critical temperature.			Volume of liquid. Critical volume.			Volume of saturated vapour. Critical volume.		
	Hexa- methylene.	Benzene.	Normal hexane.	Hexa- methylene.	Benzene.	Normal hexane.	Hexa- methylene.	Benzene.	Normal hexane.
0.001474	0.5097	0.5098	0.5263	0.3466	0.3428	—	—	—	—
0.002949	0.5354	0.5359	0.5524	0.3526	0.3489	0.3494	—	—	—
0.005898	0.5646	0.5648	0.5814	0.3597	0.3560	0.3563	—	—	—
0.011795	0.5985	0.5989	0.6144	0.3684	0.3648	0.3649	—	—	—
0.022411	0.6330	0.6334	0.6489	0.3777	0.3742	0.3746	—	—	—
0.044232	0.6759	0.6765	0.6907	0.3907	0.3870	0.3876	54.8	54.4	55.9
0.088465	0.7277	0.7282	0.7406	0.4088	0.4053	0.4053	27.7	28.2	29.1
0.14744	0.7714	0.7725	0.7831	0.4268	0.4233	0.4234	17.0	17.25	17.6
0.20642	0.8041	0.8052	0.8145	0.4424	0.4389	0.4393	12.1	12.35	12.4
0.29488	0.8428	0.8429	0.8504	0.4648	0.4602	0.4611	8.25	8.49	8.48
0.44232	0.8901	0.8906	0.8955	0.4997	0.4960	0.4964	5.28	5.35	5.36
0.58978	0.9267	0.9270	0.9308	0.5385	0.5353	0.5357	3.68	3.72	3.73
0.73721	0.9566	0.9566	0.9591	0.5873	0.5845	0.5851	2.68	2.69	2.69
0.82568	0.9720	0.9725	0.9740	0.6252	0.6250	0.6258	2.22	2.20	2.22
0.88465	0.9819	0.9824	0.9833	0.6625	0.6613	0.6612	1.91	1.91	1.92
0.94363	0.9914	0.9915	0.9922	0.7201	0.7113	0.7184	1.59	—	1.60
0.97313	0.9960	—	0.9965	0.7693	—	0.7706	1.41	—	1.41
1.00000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.00	1.00	1.00

It will be seen that the temperature ratios of hexamethylene and benzene are almost identical, those of benzene being slightly higher (maximum difference 0.0011, minimum 0.0000, mean 0.0004). The ratios for normal hexane are, however, considerably higher (maximum difference 0.0170).

As a general rule, the volume ratios for the liquid state, except near the critical point where the change of curvature is very rapid and the liability to error correspondingly great, differ much less than the temperature ratios, so that the close agreement in this respect between benzene and normal hexane is not really so significant as that just referred to between hexamethylene and benzene. It is, however, worthy of remark that the ratios for hexamethylene are higher than those for any other "normal" substance yet investigated (Report Brit. Assoc., 1898, 831) except isopentane, the agreement in the case of these two hydrocarbons being, indeed, very close.

As regards the ratios of the volumes of saturated vapour to the critical volumes, the values for benzene are, as a rule, intermediate between those for hexamethylene and for normal hexane; the differences are, however, but little greater than the probable errors of experiment.

Comparing the fifteen "normal" substances (data for two not yet published), it may be stated as a general law that if, for any substance, the temperature ratios are high, the ratios for the saturated vapour will also be high, and those for the liquid will be low, and *vice versa*. Hexamethylene forms no exception to this rule.

The most interesting comparison of the ratios of the actual to the theoretical densities of saturated vapour is at the critical point. Hexamethylene has a lower ratio than any of the other seven hydrocarbons, or, indeed, than any other substance in the "normal" group except carbon tetrachloride, and, if Amagat's results be included, carbon dioxide. The difference from the theoretical value 3.77 (Trans., 1897, 71, 452) is, however, less than 2 per cent.

In conclusion, we desire to tender our thanks to the Government Grant Committee of the Royal Society for assistance in carrying out this research.

UNIVERSITY COLLEGE, BRISTOL.

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