CIII.—*Vapour Pressures, Specific Volumes, and Critical Constants of Di*iso*propyl and Di*iso*butyl.*

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A comparison of the constants for normal and *iso*pentane (Trans., 1897, **71**, 446; *Proc. Phys. Soc.*, 1895, **13**, 602) on the one hand, and for methyl butyrate and *iso*butyrate (Trans., 1893, **63**, 1191) on the other, seemed to show that the deviations from the generalisations of van der Waals in the case of isomeric substances are intimately connected with their constitution.

In order to obtain further light on this point, it was decided to prepare specimens of di*iso*propyl and di*iso*butyl, so as to compare them with the corresponding normal paraffins.

Preparation of the Paraffins.

Specimens of these substances were first prepared by the action of sodium on *iso*propyl iodide and *iso*butyl bromide respectively in ethereal solution. No great difficulty was experienced in the preparation of di*iso*butyl, and the yield was fair. As the boiling point of the paraffin (109·2°) is considerably higher than that of *iso*butyl bromide (92·3°), it could be separated fairly completely from the unaltered bromide by fractional distillation. The final purification was effected by treatment with a mixture of nitric and sulphuric acids, and subsequent fractional distillation through a twelve-column Young and Thomas dephlegmator. Owing to the partial conversion of *iso*butyl bromide into the tertiary bromide, a small quantity of hexamethylethane is formed, but this is completely removed during the fractional distillation.

It is impossible to prepare a pure specimen of di*iso*propyl from *iso*propyl bromide, as the boiling points are almost the same, and on treatment of the mixture with nitric and sulphuric acids, bromine is set free, and at once acts on the paraffin.

Even from *iso*propyl iodide, the preparation is difficult and the yield very poor. Thus Zander (*Annalen*, 1882, **214**, 167) obtained only 5 per cent. of the theoretical yield of di*iso*propyl as against 24 per cent. of normal hexane from propyl iodide.

As has been pointed out by Silva (*Ber.*, 1872, **5**, 984), sodium has little action on a dry ethereal solution of *iso*propyl iodide, and a little water has therefore to be added. In this case, however, propylene is evolved in large quantity, and naturally carries away a good deal of the volatile hydrocarbon. We were, however, successful in obtaining a sufficient quantity of the paraffin by this method. The ether and iodide were removed for the most part by a preliminary fractionation; the rest of the ether was then dissolved out by strong sulphuric acid, and the di*iso*propyl finally completely freed from the iodide, which boils more than 30° higher, by fractional distillation through a five-column "evaporator" still-head. Several determinations of the specific gravity at 0° were made during the final stages of the fractionation, and the agreement between them, as well as the constancy of the boiling point, afforded a strong presumption in favour of the purity of the substance. Another small specimen, similarly prepared, had the same specific gravity.

It is, however, remarkable that whilst the specific gravities of the *iso*paraffins are, so far as is known, invariably lower than those of the corresponding normal hydrocarbons, and whilst di*iso*butyl is considerably lighter than normal octane, our specimen of di*iso*propyl was found to be actually heavier than normal hexane. At the same time, it may be pointed out that the specific gravities of di*iso*propyl obtained by other observers are, with one very doubtful exception, higher than ours (p. 1132).

To obtain further confirmation of the correctness of our result, it seemed desirable, if possible, to prepare a second specimen by an entirely different method.

Di*iso*propyl is stated to have been prepared by a number of reactions, which might be expected to yield normal hexane, but the products obtained, judging from the range of boiling point given, appear to have been very impure. Of the methods which do not involve a radical change in the constitution, the electrolysis of potassium *iso*butyrate seemed the most promising. In order to test the method, a preliminary preparation of di*iso*butyl from potassium *iso*valerate was made, because it seemed probable that the yield would be better, whilst the loss by evaporation would naturally be far less. As there was no doubt about the purity of our specimen of di*iso*butyl, it was not thought necessary to spend time over the purification of the *iso*valeric acid by fractional distillation, and, as a consequence, the product obtained was mixed with small quantities of its homologues or isomerides. The object of the investigation was, however, attained, inasmuch as we were able to ascertain the right conditions for a satisfactory yield of hydrocarbon. It may be mentioned that, with the apparatus used, and with a strong and slightly acid solution of the potassium salt, the yield of hydrocarbon was large compared with that of *iso*butyl *iso*valerate, or of *iso*butylene.

The electrolytic cell was similar in principle to that employed by Professor Kuenen, to whom, as well as to Professor Walker, we are indebted for valuable suggestions. The anode consisted of four rings of platinum wire about 4 cm in diameter, welded to three long, vertical platinum wires which passed above into a ∿-shaped manometer tube containing mercury, which served for making contact.

The anode was placed in a vessel constructed in the following manner. A wide-mouthed bottle was cut off a little below the neck, and for the bottom part of the bottle was substituted a porous pot of the same diameter, the surfaces of contact being carefully ground and the two portions attached by an indiarubber connection. The mouth of this vessel was provided with an indiarubber stopper perforated with two holes, through one of which passed the ∿-shaped tube, and through the other a vertical exit tube for gases. The cathode, of stout amalgamated zinc, and the porous pot which it nearly surrounded, were placed in a wide, cylindrical, glass vessel, which during the experiment was cooled by ice. The current used was about 6·5 amperes, and the voltage nearly 10.

A 30 to 35 per cent. solution of caustic potash was neutralised with *iso*valeric acid, and a little more acid added. The porous pot and outer vessel were filled with the solution, and the current was passed for about 3 hours in each operation. The amount of *iso*butylene was roughly estimated by absorption in bromine, after removal of the carbon dioxide.

The oil from the porous cell was separated and distilled through a "pear" still-head with twelve bulbs, and was found to consist of di*iso*butyl, *iso*butyl *iso*valerate, and free *iso*valeric acid. The portion boiling from about 108° to 120° amounted, on an average, to about 7·5 grams in each operation. The total quantity, 45·2 grams, resulting from about 18 hours' electrolysis, was treated with potash to remove free acid, boiled with strong potash to hydrolyse any ester, washed with water, shaken twice with strong sulphuric acid, and finally washed with water, dried with phosphoric oxide, and distilled through a five-column "evaporator" still-head. Very nearly 10 grams were collected between 109·15° and 109·2° (corr. to 760 mm.), and a second 10 grams from 109·2° to 109·25°. The specific gravities at 0° were 0·71066 and 0·71092 respectively, that of the pure specimen obtained from *iso*butyl bromide being 0·71021. Considering that the quantity of di*iso*butyl prepared was insufficient for complete purification by fractional distillation, the agreement may be regarded as satisfactory. The amount of *iso*butyl *iso*valerate was estimated by neutralising the distillate from 120° to 176°, so as to remove free acid.

With a view to the preparation of a pure specimen of di*iso*propyl by the electrolytic method, a kilogram of *iso*butyric acid, supplied by

Kahlbaum, was carefully fractionated with a "pear" still-head, 780 grams of the acid, boiling within 0·05°, being obtained. The strength of the solution, the current, and the electrolytic cell were the same as in the case of potassium *iso*valerate, but owing to the fact that the quantity of di*iso*propyl formed was so small as to be almost entirely carried forward by the gases evolved in the porous pot, it was found necessary to devise a method for absorbing the carbon dioxide and propylene without injuring or losing the di*iso*propyl. The absorbents finally used were a strong solution of caustic potash and strong sulphuric acid. The former was contained in a nearly horizontal absorption tube provided with safety bulbs at either end, and a short, narrow tube with a stop-cock for running off the liquid and separating any oil at the end of the experiment. The acid was contained in a sloping tube with eighteen small bulbs; this was similarly provided with large safety bulbs and stoppered exit tube. The absorption of both carbon dioxide and propylene was practically complete.

During each operation, it was found that a very small quantity of oil collected on the surface of the potash, and a relatively much larger quantity over the sulphuric acid. These were accumulated in separate small flasks, to be worked up when the quantity was sufficient.

The liquid from the porous pot was not placed in a separating funnel on account of the volatility of the paraffin, but was distilled each time until the temperature reached about 98°, the distillate being collected in a tube cooled by a freezing mixture.* This was found convenient, for the water that came over froze, and the oil could be poured from the ice with scarcely any loss.

The sulphuric acid from the absorption tube, in the first two or three cases, was diluted and distilled in a similar manner, but the quantity of di*iso*propyl was inappreciable, the distillate consisting of *iso*propyl alcohol, together with polymerides of propylene in small quantity, most of the latter, however, remaining behind in the distilling flask. After obtaining a sufficient quantity of *iso*propyl alcohol to identify it, the treatment of the sulphuric acid was discontinued. There were thus, at the end of the operations, three quantities of oil to work up: A, that from the porous pot; B, that from the potash tube; C, that from the sulphuric acid bulbs.

A. The liquid was distilled through the five-column "evaporator" still-head until the temperature rose to 80°, in order to separate any di*iso*propyl. The residue, kept cool by running water, was mixed with strong sulphuric acid, in which it dissolved completely. After standing for some time, it was diluted, and the oil that separated was

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* In order to avoid loss of di*iso*propyl by evaporation during the various processes involved in its isolation, the receivers were in all cases cooled by freezing mixtures.

removed, treated with caustic soda, washed with water, and, lastly, dried and freed from any remaining *iso*propyl alcohol by the repeated addition of small quantities of phosphoric oxide until the latter remained in a floury condition. It was then distilled from phosphoric oxide and fractionated with a "pear" still-head. The weight of *iso*propyl *iso*butyrate, boiling from about 117° to 125°, was 38 grams, and from this 21 grams of ester, boiling constantly at 120·75°, was obtained.

B. The distillate from A boiling below 80° was mixed with B. It was found to be almost completely soluble in strong sulphuric acid, and the small remaining layer boiled between 56° and 70°, mostly at 58°, and consisted, therefore, mainly of di*iso*propyl. The ester, which separated on dilution of the sulphuric acid solution, was found to be practically free from di*iso*propyl.

C. This oil was first distilled with steam; the quantity that came over below about 90° was disappointingly small, a considerable amount of heavy oil, consisting, doubtless, of polymerides of propylene, remaining in the flask. The distillate, separated from the water and dried, was redistilled, and the portion boiling within about the same limits of temperature was collected with the di*iso*propyl from B. The total weight was only 3·4 grams. A relatively large amount of di*iso*propyl was lost in the preliminary experiments, but, even under the best conditions, 100 grams of isobutyric acid gave only 1·5 grams of moderately pure di*iso*propyl, the theoretical yield being 49 grams.*

The crude paraffin was dried with a little phosphoric oxide and redistilled, when it boiled from 57·6° to 62·5°, the greater part coming over at about 58°. The weight was now 2·6 grams, and the specific gravity at 0° was found to be 0·6811, as against 0·6797 for the specimen prepared from *iso*propyl iodide, when determined in the same small apparatus.

The di*iso*propyl was redistilled three times from a little phosphoric oxide, the temperature not rising higher the last time than 58·8°, and remaining fairly constant at about 58·0° during the greater part of the distillation. The specific gravity at 0° had now fallen to 0·6806, and it is evident that further redistillation would not have lowered it below that found for the other specimen. Inasmuch as polymerides of propylene were formed in presence of the strong sulphuric acid, it was still possible that a hexylene, boiling at about the same temperature as di*iso*propyl, might be present. It was found, however, that the

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* Dr. J. Petersen, of Copenhagen, states (*Bull. Acad. roy. Danemark*, 1897, 397; *Zeit. physikal. Chem.*, 1900, **33**, 99) that the yield of di*iso*propyl obtained by the electrolysis of potassium *iso*butyrate is exceedingly small compared with that of *iso*propyl *iso*butyrate from the same salt, or of normal hexane from potassium butyrate.

small residues from the later distillations referred to had practically no decolorising action on bromine.

The main object of the investigation was therefore attained, since it was proved that the specific gravity of pure di*iso*propyl is not really lower than that obtained for the specimen from *iso*propyl iodide.

THERMAL CONSTANTS OF DI*ISO*PROPYL.

These constants were determined with the specimen from *iso*propyl iodide, that from potassium *iso*butyrate being too small and not sufficiently pure.

Boiling Point.

Both hydrocarbons were distilled from phosphoric oxide immediately before being used for the determinations of specific gravity, vapour pressures, &c. There are, therefore, several observations of the boiling point of each substance.

Pressure.	Temperature.	
	Observed.	Corrected to 760 mm.
755·6	57·85°	58·05°
753·9	57·80	58·05
752·3	57·75	58·05
753·3	57·9	58·15
	Mean	58·08

Calculated from the constants for Biot's formula, the boiling point is 58·10°, and the value of dp/dt at the boiling point is 24·26 mm. per degree.

Boiling points given by other observers.

Name.	Reference.	Boiling point.
Schorlemmer...	*Annalen*, 1867, **144**, 184.	58°
Zander	*Annalen*, 1882, **214**, 167.	58
Engler	*Ber.*, 1889, **22**, 595.	57—59
Riche	*Ann. Chim. Phys.*, 1860, [iii], **59**, 426.	56—58
Aschan	*Ber.*, 1898, **31**, 1801.	57—59

Schorlemmer's and Zander's specimens were prepared from *iso*propyl iodide and sodium; Engler's from whale oil by destructive distillation; Riche's by heating œnanthylic acid with barium oxide, whilst Aschan's was separated from Baku petroleum.

Specific Gravity.

The specific gravities of two different specimens were determined at 0°/4° in a Sprengel tube as modified by Perkin; the weighings were reduced to a vacuum.

A......	0·67951
B......	0·67945
Mean	0·67948

Specific gravities by other observers.

	Specific gravity.	
	At *t*.	Reduced to 0°/4.
Schorlemmer	0·6769 at 10°	0·6857
	0·6701 „ 17·5	0·6858
	0·6569 „ 29·0	0·6831
Zander..............	0·6680 „ 17·5	0·6829
Engler..............	0·6677 „ 21	0·6867
Riche		0·668
Aschan	0·66485 „ 17·25	0·68173

There is some uncertainty about the reductions to 0°, as it is usually not stated whether the specific gravity is referred to water at 4°, at 0°, or at the same temperature (*t*) as that of the substance. We have assumed that the water was at 4° in each case. If it had been at *t*°, the reduced specific gravities would be slightly lower; thus Engler's would be 0·6853 instead of 0·6867.

The determination by Riche differs entirely from all the others, but many of the results described in his paper, such as the existence of a hexane boiling at 78°, are difficult to explain, and it seems most improbable that di*iso*propyl could be obtained from œnanthylic acid as he describes. Of the other results, those of Aschan and Zander agree best with ours, both being a little higher.

Vapour Pressures at Low Temperatures.

For pressures up to 320 mm., the method of Ramsay and Young was employed; from 240 mm. to the atmospheric pressure, a modified distillation bulb provided with a reflux condenser was used.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
36·8 mm.	−13·5°	64·45 mm.	−3·4°	138·5 mm.	12·6°	238·7 mm.	25·55°
39·4	−12·45	77·9	+0·4	167·2	17·1	259·0	27·75
41·6	−11·45	92·25	3·85	200·2	21·25	278·5	29·5
51·65	− 7·4	112·2	8·25	219·8	23·6	299·5	31·4
242·65	25·65	324·9	33·25	444·2	41·9	591·4	50·4
262·5	27·70	362·3	36·25	488·8	44·65	646·6	53·3
291·1	30·35	403·2	39·2	538·7	47·55	694·3	55·35

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

$$\log.p = a + ba^t + c\beta^t,$$

are given in the following table.

The constants for Biot's formula are :

$$a = 14{\cdot}002278$$

$$b = -10{\cdot}645849 \qquad \log.\ b = 1{\cdot}0271804$$

$$c = -\ 1{\cdot}699429 \qquad \log.\ c = 0{\cdot}2303031$$

$$\log.\ a = \bar{1}{\cdot}99979200$$

$$\log.\ \beta = \bar{1}{\cdot}99533068$$

$$t = t^\circ C + 10.$$

Vapour pressures.

Temperature.	Dynamical method from curve.	Statical method.	Calculated from Biot's formula.	Temperature.	Statical method.	Calculated from Biot's formula.
−10°	45·20 mm.		45·4 mm.	140°	5717 mm.	5697 mm.
0	75·95		76·05	150	6884	6879
10	123·45		122·25	160	8256	8234
20	190·55		189·4	170	9806	9781
30	285·1		283·8	180	11535	11536
40	411·6		412·6	190	13475	13519
50	584·8		584·1	200	15693	15752
60		807 mm.	806·8	210	18208	18258
70		1093	1090·3	216	19848	—
80		1444	1444·8	220	21009	21062
90		1876	1880·9			
100		2411	2409·7	225	22588	—
110		3044	3043·0			
120		3790	3793·2	227·35 (critical)	23360	23330
130		4677	4673			

The critical temperature was taken to be 227·40°, and the critical pressure 23,345 mm.

Volumes of a Gram of Liquid.

These were determined in the pressure apparatus; up to 150°, 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 previously described by one of us (Trans., 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. The molecular weight is taken as 85·82.

Volumes of a gram and molecular volumes of liquid.

Temp.	Volumes of a gram in c.c.		Molecular volumes. in c.c.	Temp.	Volumes of a gram in c.c.		Molecular volumes in c.c.
	Observed.	From curve.			Observed.	From curve.	
0°	1·4717	1·4717	126·30	140°	1·8744	1·8748	160·89
10	—	1·4909	127·95	150	1·9236	1·9240	165·12
20	—	1·5113	129·70	160	1·9813	1·9805	169·95
30	1·5327	1·5326	131·53	170	2·0482	2·0470	175·70
40	1·5551	1·5547	133·43	180	2·1260	2·1255	182·40
50	1·5775	1·5777	135·40	190	2·2149	2·2185	190·40
60	1·6018	1·6019	137·48	200	2·3394	2·3395	200·80
70	1·6270	1·6276	139·68	210	2·5070	2·5075	215·20
80	1·6568	1·6559	142·11	216	2·6610	2·6610	228·35
90	1·6866	1·6860	144·69	220	2·8048	2·8050	240·70
100	1·7182	1·7180	147·44	223	2·9660	2·9660	254·55
110	1·7517	1·7520	150·36	225	3·1263	3·1265	268·30
120	1·7889	1·7891	153·54	226·5	3·3699	3·3700	289·20
130	1·8307	1·8300	157·05	227·4 (critical)	—	4·148*	356·0*

* By the method of Cailletet and Mathias corrected for the slight curvature of the "diameter."

Volumes of a Gram of Saturated Vapour.

Determinations were made with the pressure apparatus and by the sealed tube method (Trans., 1891, **59**, 37; *Proc. Phys. Soc.*, 1895, **13**, 617).

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 in c.c.				Molecular volumes in c.c.
	Pressure apparatus.	Sealed tube method.		From curves.	
		I.	II.		
50			379	392	33600
60			294	290	24900
70			219	219	18780
80			166	166·5	14290
90			129·0	129·0	11070
100			101·0	101·0	8670
110		75·2	80·1	80·0	6865
120		63·0	64·3	64·3	5515
130		51·4	51·9	52·0	4465
140		40·5		42·4	3635
150		34·3		35·4	3040
160	28·4	28·0		28·4	2440
170	23·25	23·35		23·30	2000
180	19·12	19·16		19·17	1645
190	15·76	15·64		15·72	1349
200	12·76	12·72		12·77	1095
210	10·15	10·13		10·14	870
216	8·61	8·64		8·60	738
220	7·575	7·57		7·57	650
223	6·710	6·74		6·72	577
225	6·065	—		6·065	520
226·5	5·400	—		5·410	464
227·4 (critical.)				4·148*	356·0*

* By the method of Cailletet and Mathias corrected for the slight curvature of the "diameter."

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, taking into account the fact that the "diameter" is very slightly curved.

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

$$D_t = 0{\cdot}3401 - 0{\cdot}0004445t + 0{\cdot}0000000413t^2$$

are given below.

The densities of saturated vapour below 50° were calculated from the vapour pressures on the assumption that the vapour densities are normal. The density at the critical point, calculated from the above formula, is 0·2411; from the simpler formula,

$$D_t = 0{\cdot}3395 - 0{\cdot}000433t,$$

it would be 0·2410. The difference is thus exceedingly small at the critical point, but would be much more marked at the lowest temperatures.

Temperature.	Densities.		Mean densities.		
	Liquid.	Saturated vapour.	Observed.	Calculated.	$\Delta \times 10^4$
0°	0·6795	0·0004	0·3399	0·3401	+2
10	0·6707	0·0006	0·3357	0·3357	0
20	0·6617	0·0009	0·3313	0·3312	−1
30	0·6525	0·0013	0·3269	0·3268	−1
40	0·6432	0·0018	0·3225	0·3224	−1
50	0·6338	0·0026	0·3182	0·3180	−2
60	0·6243	0·0034	0·3138	0·3136	−2
70	0·6144	0·0046	0·3095	0·3092	−3
80	0·6039	0·0060	0·3050	0·3048	−2
90	0·5931	0·0077	0·3004	0·3004	0
100	0·5821	0·0099	0·2960	0·2960	0
110	0·5708	0·0125	0·2916	0·2917	+1
120	0·5589	0·0156	0·2873	0·2874	+1
130	0·5464	0·0192	0·2828	0·2830	+2
140	0·5334	0·0236	0·2785	0·2787	+2
150	0·5197	0·0282	0·2740	0·2743	+3
160	0·5049	0·0352	0·2701	0·2701	0
170	0·4885	0·0429	0·2657	0·2657	0
180	0·4705	0·0522	0·2614	0·2614	0
190	0·4508	0·0636	0·2572	0·2571	−1
200	0·4274	0·0784	0·2529	0·2529	0
210	0·3988	0·0986	0·2487	0·2486	−1
216	0·3758	0·1163	0·2460	0·2460	0
220	0·3565	0·1321	0·2443	0·2443	0
223	0·3372	0·1488	0·2430	0·2431	+1
225	0·3198	0·1650	0·2424	0·2422	−2
226·5	0·2967	0·1849	0·2408	0·2415	+7
227·4	—	—	—	0·2441	

THERMAL CONSTANTS OF DI*iso*BUTYL.

The constants were determined with the specimen prepared by the action of sodium on *iso*butyl bromide.

Boiling point.

Pressure.	Temperature.	
	Observed.	Corrected to 760 mm.
748·65	108·65°	109·2°
752·3	108·85	109·2
746·5	108·6	109·25
	Mean	109·2

From Biot's formula, b. p. = 109·2°; $dp/dt = 20{\cdot}9$ mm. per degree at the b. p.

Boiling points given by other observers :

Name.	Reference.	Boiling Point. Observed.	Boiling Point. Corrected to 760 mm.
Kolbe......	*Annalen*, 1849, **69**, 259		108°
Kopp	*Annalen*, 1855, **95**, 335	108·5° at 747·5	109·1
Thorpe ...	Trans., 1880, **37**, 219	108·2—108·7° at 748·2	108·53
Schiff	*Annalen*, 1883, **220**, 88	107·8—107·9° at 751·4	108·25
Williams ..	*Annalen*, 1879, **35**, 125	108·2° at 745	108·9
Pawlewski	*Ber.*, 1883, **16**, 2634		107·5

Kolbe's specimen was obtained by the electrolysis of potassium *iso*valerate. Most, if not all, of the others were prepared by the action of sodium on *iso*butyl bromide or iodide. Kopp's result agrees best with ours.

Specific gravity.

Temperature.	Specific gravity.
0°/4°	0·71021
11·9°/4°	0·69996

Specific gravities determined by other observers.

Name.	Reference.	Specific gravity at *t*°.	Specific gravity Calculated at 0°/4°.
Kolbe	.........*Jahresb.*, 1848, **1**, 559	0·6940 at 18°	0·7091
Wurtz	.........*Jahresb.*, 1855, **8**, 576		0·7057
Kopp	............*loc. cit.*		0·7135
Williams	......*loc. cit.*		0·7091 0·7085
Schorlemmer	...*Jahresb.*, 1867, **20**, 567	0·698 at 16·5°	0·7119
Thorpe	.........*loc. cit.*		0·7111
Schiff	...........*loc. cit.*	0·7001 at 12·1°/4°	0·7103

Most of the above results are in fair agreement with ours, that of Schiff differing only slightly.

Vapour pressures at low temperatures.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
8·70 mm.	3·55°	16·65 mm.	14·35°	38·15 mm.	29·85°	84·8 mm.	47·3°
9·50	4·75	19·3	16·7	45·35	33·45	96·2	50·3
10·70	6·75	22·4	19·65	53·85	37·15	108·8	53·3
12·00	8·6	28·4	24·2	61·85	40·05	122·5	56·15
13·9	11·2	32·35	26·55	72·5	43·6	138·45	59·1
158·25	62·05	248·0	73·95	373·2	86·0	552·2	98·25
177·55	65·05	278·3	77·25	410·8	88·9	603·2	101·3
197·6	67·85	307·0	80·05	455·3	92·15	657·0	104·25
221·8	70·9	339·6	83·05	501·5	95·2	715·2	107·2

Constants for Biot's formula.

$a = 2{\cdot}918091$

$b = 0{\cdot}846986$ $\qquad \log. b = \bar{1}{\cdot}9278763$

$c = -2{\cdot}628903$ $\qquad \log. c = 0{\cdot}4197746$

$\log. \alpha = 0{\cdot}00104426$

$\log. \beta = \bar{1}{\cdot}99619775$

$t = t^{\circ}C - 10$

Vapour pressures.

Temperature	Dynamical method from curve.	Statical method.	Calculated from Biot's formula.	Temperature.	Statical method.	Calculated from Biot's formula.
0°	—		7·11	150°	2116	2118·2
10	13·0		13·0	160	2645	2630·6
20	23·05		22·77	170	3243	3231·3
30	38·5		38·19	180	3938	3930·2
40	61·8		61·68	190	4740	4738·0
50	95·95		96·19	200	5670	5666·5
60	145·2		145·35	210	6733	6729·5
70	213·3		213·3	220	7937	7941
80	305·5		304·9	230	9312	9319
90	426·6		425·6	240	10905	10883
100	578·8		581·15	250	12668	12654
110	777·1		777·9	260	14651	14660
120		1020	1022·6	270	16905	16929
130		1319	1322·5	276·8 (critical)	18660	18640
140		1685	1684·9			

Volumes of a gram and molecular volumes of liquid.

Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.	Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.
	Observed.	From curve.			Observed.	From curve.	
0°	1·4080	1·4080	160·17	150°	1·7438	1·7447	198·48
10	—	1·4248	162·08	160	1·7791	1·7795	202·44
20	—	1·4422	164·07	170	1·8169	1·8172	206·72
30	1·4595	1·4602	166·11	180	1·8573	1·8577	211·35
40	1·4785	1·4784	168·57	190	1·9028	1·9030	216·50
50	1·4975	1·4977	170·38	200	1·9526	1·9542	222·30
60	1·5165	1·5170	172·57	210	2·015	2·0120	228·90
70	1·5364	1·5376	174·92	220	2·077	2·0792	236·55
80	1·5570	1·5583	177·27	230	2·158	2·1585	245·55
90	1·5802	1·5803	179·78	240	2·255	2·2555	256·60

* The molecular weight was taken to be 113·76.

Volumes of a gram and molecular volumes of liquid—(continued).

Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.	Temp.	Volumes of a gram in c.c.		* Molecular volumes in c.c.
	Observed.	From curve.			Observed.	From curve.	
100	1·6044	1·6036	182·43	250	2·380	2 3805	270·80
110	1·6293	1·6280	185·20	260	2·556	2·5560	290·75
120	1·6543	1·6540	188·16	270	2·871	2·8710	326·60
130	1·6810	1·6821	191·36	274	3·137	3·1370	356·85
140	1·7137	1·7122	194·78	276·8 (critical)	—	4·227 †	480·8 †

Volumes of a gram and molecular volumes of saturated vapour.

Temperature.	Volumes of a gram in c.c.				Molecular volumes in c.c.
	Pressure apparatus.	Sealed tube method.		From curves.	
		I.	II.		
90°			443	460	52400
100			339	337	38300
110			255	251	28600
120			194	191	21800
130			147·1	148	16800
140			117·0	117·2	13340
150			93·7	93·3	10620
160			75·3	75·8	8630
170			62·0	62·1	7060
180			51·6	51·1	5810
190		42·5	42·2	42·2	4800
200		34·8		34·8	3960
210	28·45	28·8		28·7	3270
220	23·91	23·8		23·8	2707
230	19·60	19·6		19·63	2234
240	16·07	16·08		16·07	1828
250	13·03	12·95		13·02	1481
260	10·31	10·26		10·31	1172
270	7·565	7·61		7·57	861
274	6·36	6·36		6·36	723
276·8 (critical)	—			4·227 †	480·8 †

* The molecular weight was taken to be 113·76.

† By the method of Cailletet and Mathias, corrected for the slight curvature of the "diameter."

In the following table, the calculated densities are obtained from the formula

$$D_t = 0{\cdot}3550 - 0{\cdot}0004115t - 0{\cdot}0000000592t^2.$$

The density at the critical point, calculated from this formula, is 0·2366; from the simpler formula

$$D_t = 0{\cdot}3567 - 0{\cdot}000433t,$$

it would be 0·2369. The difference is small, but would be considerable at the lowest temperatures.

Temperature.	Densities.		Mean densities.		
	Liquid.	Saturated vapour	Observed.	Calculated.	$\Delta \times 10^4$
0	0·7102	0·0000	0·3551	0·3550	−1
10	0·7019	0·0001	0·3510	0·3509	−1
20	0·6934	0·0002	0·3468	0·3468	0
30	0·6848	0·0002	0·3425	0·3426	+1
40	0·6764	0·0004	0·3384	0·3384	0
50	0·6677	0·0005	0·3342	0·3343	+1
60	0·6592	0·0008	0·3300	0·3301	+1
70	0·6504	0·0012	0·3258	0·3259	+1
80	0·6417	0·0016	0·3217	0·3217	0
90	0·6328	0·0022	0·3175	0·3175	0
100	0·6236	0·0030	0·3133	0·3132	−1
110	0·6143	0·0040	0·3091	0·3090	−1
120	0·6046	0·0052	0·3049	0·3047	−2
130	0·5945	0·0068	0·3006	0·3005	−1
140	0·5841	0·0085	0·2963	0·2962	−1
150	0·5732	0·0107	0·2919	0·2920	+1
160	0·5620	0·0132	0·2876	0·2877	+1
170	0·5503	0·0161	0·2832	0·2833	+1
180	0·5383	0·0196	0·2789	0·2790	+1
190	0·5255	0·0237	0·2746	0·2747	+1
200	0·5117	0·0287	0·2702	0·2703	+1
210	0·4970	0·0349	0·2659	0·2660	0
220	0·4810	0·0420	0·2615	0·2616	+1
230	0·4633	0·0509	0·2571	0·2573	+2
240	0·4434	0·0622	0·2528	0·2528	0
250	0·4199	0·0769	0·2484	0·2484	0
260	0·3912	0·0970	0·2441	0·2440	−1
270	0·3482	0·1322	0·2402	0·2396	−6
274	0·3187	0·1574	0·2380	0·2378	−2
276·8 (critical)	—			0·2366	

THEORETICAL CONCLUSIONS.

The absolute temperatures and the molecular volumes of the two hydrocarbons, both as liquid and as saturated vapour, were read from the curves at the usual series of "reduced pressures"; 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 normal and *iso*pentane, normal hexane, and normal octane are added.

Reduced pressures.	Pressures.		Absolute temperatures.		Molecular volumes.			
					Liquid.		Saturated vapour.	
	Di*iso*-propyl.	Di*iso*-butyl.	Di*iso*-propyl.	Di*iso*-butyl.	Di*iso*-propyl.	Di*iso*-butyl.	Di*iso*-propyl.	Di*iso*-butyl.
0·000590	—	11·0	—	280·25	—	161·55	—	—
0·001474	34·40	27·5	258·2	296·25	—	164·75	—	—
0·002949	68·85	55·0	270·85	310·45	—	167·64	—	—
0·005898	137·7	110·05	285·4	326·2	128·37	171·06	—	—
0·011795	275·4	220·1	302·2	343·75	131·38	175·08	—	—
0·022411	523·2	418·2	319·8	362·5	134·75	179·64	—	—
0·044232	1033	825·4	341·2	386·1	139·26	185·79	19750	26900
0·088465	2065	1651	366·75	412·25	145·71	194·52	10130	13520
0·14744	3442	2751	388·5	434·95	152·07	203·25	6085	8290
0·20642	4819	3852	404·35	451·85	157·58	210·80	4330	5940
0·29488	6884	5502	422·95	471·25	165·05	221·25	2979	4090
0·44232	10326	8254	446·0	495·3	177·60	238·55	1888	2580
0·58978	13768	11005	464·25	513·5	191·60	257·40	1314	1811
0·73721	17210	13755	479·05	528·4	208·75	280·65	957	1312
0·82568	19275	15405	486·9	536·3	223·15	300·00	786	1067
0·88465	20650	16505	491·75	541·15	236·80	317·95	679	984
0·94363	22030	17610	496·15	545·75	255·75	344·80	572	773
0·97313	22715	18160	498·45	548·0	273·75	—	505	—
1·00000	23345	18660	500·4	549·8	356·0	480·8	356·0	480·8

Reduced pressures.	$\frac{\text{Volume of saturated vapour.}}{\text{Critical volume.}}$						$\frac{\text{Densities of saturated vapour.}}{\text{Theoretical density.}}$					
	*iso*Pentane.	*n*-Pentane.	Di*iso*propyl.	*n*-Hexane.	Di*iso*butyl.	*n*-Octane.	*iso*Pentane.	*n*-Pentane.	Di*iso*propyl.	*n*-Hexane.	Di*iso*butyl.	*n*-Octane.
0·044232	53·4	54·3	55·5	55·9	56·0	56·1	1·070	1·069	1·040	1·069	1·080	1·099
0·088465	27·7	28·4	28·4	29·1	28·2	29·3	1·111	1·098	1·089	1·103	1·148	1·128
0·14744	16·9	17·0	17·1	17·6	17·3	17·9	1·159	1·166	1·153	1·153	1·185	1·167
0·20642	12·0	12·1	12·2	12·4	12·4	12·7	1·215	1·217	1·204	1·218	1·228	1·218
0·29488	8·29	8·35	8·37	8·48	8·50	8·67	1·289	1·294	1·282	1·302	1·302	1·300
0·44232	5·27	5·27	5·30	5·36	5·37	5·43	1·427	1·439	1·421	1·445	1·446	1·452
0·58978	3·69	3·68	3·69	3·73	3·77	3·79	1·588	1·610	1·595	1·621	1·601	1·617
0·73721	2·65	2·68	2·69	2·69	2·73	2·73	1·825	1·826	1·807	1·851	1·819	1·852
0·82568	2·19	2·21	2·21	2·22	2·22	2·23	2·007	2·010	1·996	2·034	2·028	2·049
0·88465	1·89	1·90	1·91	1·92	1·92	—	2·186	2·204	2·180	2·219	2·213	—
0·94363	1·58	1·59	1·61	1·60	1·61	—	2·488	2·484	2·450	2·517	2·493	—
0·97313	1·39	1·40	1·42	1·41	1·40	—	2·754	2·759	2·698	2·774	—	—
1·00000	1·00	1·00	1·00	1·00	1·00	1·00	3·733	3·762	3·742	3·831	3·808	3·863

Reduced pressures.	Absolute temperature / Absolute critical temperature						Volume of liquid / Critical volume					
	*iso*Pentane.	*n*-Pentane.	Di*iso*propyl.	*n*-Hexane.	Di*iso*butyl.	*n*-Octane.	*iso*Pentane.	*n*-Pentane.	Di*iso*propyl.	*n*-Hexane.	Di*iso*butyl.	*n*-Octane.
0·000590	—	—	—	0·4965	0·5097	0·5165	—	—	—	—	0·3360	0·3317
0·001474	—	—	0·5160	0·5263	0·5388	0·5462	—	—	—	—	0·3426	0·3383
0·002949	0·5366	0·5414	0·5413	0·5524	0·5647	0·5714	—	—	—	0·3496	0·3487	0·3443
0·005898	0·5660	0·5707	0·5703	0·5814	0·5933	0·5995	—	—	0·3606	0·3565	0·3558	0·3513
0·011795	0·5994	0·6040	0·6039	0·6144	0·6252	0·6313	0·3683	0·3660	0·3690	0·3650	0·3641	0·3597
0·022411	0·6346	0·6396	0·6391	0·6489	0·6593	0·6650	0·3778	0·3755	0·3786	0·3747	0·3736	0·3693
0·044232	0·6777	0·6824	0·6819	0·6907	0·7023	0·7060	0·3908	0·3885	0·3912	0·3877	0·3864	0·3826
0·088465	0·7292	0·7331	0·7329	0·7406	0·7498	0·7544	0·4084	0·4062	0·4094	0·4055	0·4046	0·4006
0·14744	0·7732	0·7769	0·7764	0·7831	0·7911	0·7954	0·4262	0·4244	0·4272	0·4236	0·4227	0·4186
0·20642	0·8059	0·8091	0·8081	0·8145	0·8217	0·8255	0·4419	0·4399	0·4427	0·4395	0·4384	0·4345
0·29488	0·8434	0·8460	0·8452	0·8504	0·8571	0·8598	0·4634	0·4612	0·4637	0·4613	0·4602	0·4560
0·44232	0·8902	0·8917	0·8913	0·8955	0·9009	0·9026	0·4987	0·4974	0·4990	0·4966	0·4962	0·4932
0·58978	0·9266	0·9278	0·9277	0·9308	0·9340	0·9352	0·5386	0·5378	0·5383	0·5360	0·5353	0·5324
0·73721	0·9566	0·9574	0·9573	0·9591	0·9611	0·9619	0·5881	0·5869	0·5865	0·5853	0·5837	0·5818
0·82568	0·9722	0·9727	0·9730	0·9740	0·9755	0·9758	0·6272	0·6265	0·6269	0·6261	0·6239	0·6243
0·88465	0·9800	0·9826	0·9827	0·9833	0·9843	0·9845	0·6653	0·6635	0·6652	0·6615	0·6613	—
0·94363	0·9918	0·9916	0·9915	0·9922	0·9926	0·9926	0·7229	0·7197	0·7185	0·7187	0·7168	—
0·97313	0·9963	0·9963	0·9961	0·9965	0·9967	0·9965	0·7751	0·7724	0·7691	0·7710	—	—
1·00000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000

From the foregoing tables, it will be seen that the ratios of (*a*), the absolute temperatures to the absolute critical temperatures, (*c*) the volumes of saturated vapour to the critical volumes, (*d*) the actual to the theoretical densities, are higher for the normal paraffins than for their isomerides; the exceptions are slight, and are mostly near the critical points; including the cases where the ratios are equal, there are only 4 exceptions out of 51 comparisons under *a*, 6 out of 33 under *c*, and 8 out of 36 under *d*. On the other hand, the ratios (*b*) of the volumes of liquid to the critical volumes are lower for the normal paraffins than for the corresponding *iso*- or di*iso*-compounds; the exceptions are very slight, and only number 3 out of 44.

Comparing methyl butyrate with methyl *iso*butyrate, the ratios *a*, *b*, and *c* show differences in the same direction as above (exceptions, 4 out of 18, 0 out of 18, and 0 out of 12 respectively), but the ratios of the actual to the theoretical densities exhibit great irregularity, only 6 out of 13 being higher for the normal than for the *iso*butyrate.

We may therefore conclude, with regard to the ratios *a*, *b*, and *c*, that the statements made above represent general laws, but in the case of the ratios *d* the differences are too small, compared with the experimental errors, to allow of any very certain deduction being drawn.

Lastly, it may be interesting to compare the critical and some other constants of the same six hydrocarbons, in order to obtain some light on the relative influence of the single and double *iso*-groups.

Name.	B. p. 760 mm.	Δ	Sp. gr. 0°/4°	Δ	Crit. temp.	Δ
*iso*Pentane . .	27·95°	−8·35°	0·63930	−0·00609	187·8°	−9·4
Normal pentane	36·3		0·64539		197·2	
Di*iso*propyl . .	58·1	−10·85	0·67948	+0·00251	227·4	−7·4
Normal hexane.	68·95		0·67697		234·8	
Di*iso*butyl . .	109·2	−14·6	0·71021	−0·00827	276·8	−19·4
Normal octane .	125·8		0·71848		296·2	

Name.	Crit. pressure.	Δ	Crit. density.	Δ	$\frac{Dc}{D'c}$ *	Δ
*iso*Pentane . .	25020	−80	0·2343	+0·0020	3·732	−0·030
Normal pentane	25100		0·2323		3·762	
Di*iso*propyl . .	23345	+835	0·2411	+0·0067	3·742	−0·089
Normal hexane.	22510		0·2344		3·831	
Di*iso*butyl . .	18660	−70	0·2366	+0·0039	3·808	−0·049
Normal octane .	18730		0·2327		3·863	

* $\frac{Dc}{D'c}$ = the ratio of the actual to the theoretical density at the critical point.

Comparing the di*iso*butyl and normal octane differences with those of normal and *iso*pentane, it will be seen that the double *iso*-group has, in most cases, approximately twice the effect of the single in altering the properties. Whilst, however, the specific gravity at 0° and the critical pressure of the isomeride are in each case lower than those of the normal paraffin, the difference between the influence of the *iso*- and di*iso*-groups is here slight.

A comparison of the constants for methyl *iso*butyrate and methyl butyrate shows that the differences are the same in sign, and not very different in amount from those existing in the case of the pentanes.

As regards di*iso*propyl and normal hexane, it appears evident that something beyond the mere presence of the di*iso*-group in the former substance must be taken into account, for in the comparison of their differences with those of the pentanes (or octanes), great irregularities are to be observed. Thus, the critical pressure and the specific gravity of di*iso*propyl are both higher than those of normal hexane, instead of lower. It is somewhat remarkable that the critical densities of the *iso*- and di*iso*-compounds are in all four cases higher than those of the normal substances, but this peculiarity is greatly accentuated with di*iso*propyl.

From the difficulty experienced in preparing this hydrocarbon, it would seem that the $(CH_3)_2CH-$ groups show considerably less tendency to unite together than those alkyl groups which are not of the form $\begin{matrix}R\\R'\end{matrix}\!\!>CH-$. Thus, when potassium *iso*valerate was electrolysed, the amount of di*iso*butyl formed was very large compared with that of *iso*butyl *iso*valerate; whereas, under similar conditions, potassium *iso*butyrate gave a relatively much larger yield of *iso*propyl *iso*butyrate than of di*iso*propyl.

It seems probable that the peculiarities of di*iso*propyl may, in some way, be due to the fact that there are two CH groups attached to one another in the molecule.

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