XXXIV.—*The Critical Temperature and Value of* $\frac{ML}{\Theta}$ *of some Carbon Compounds.*

By James Campbell Brown, D.Sc.

In two former papers (Trans., 1903, **83**, 991, and 1905, **87**, 269) on the determination of latent heat, the author was not able to calculate the value of $\frac{ML}{\Theta}$ for some of the compounds because the critical temperature had not been determined, or at least was not recorded in any available journal.

Having a sufficient supply of very pure substances, it seemed desirable to make the determination of critical temperature, as well for the purpose of recording this constant itself as for the purpose of calculating the value $\frac{ML}{\Theta}$.

Method.—Tubes of soda glass were prepared about 4·5 cm. long having between 4 and 5 mm. internal diameter, the walls being 2 mm. thick. The tubes were sealed at one end and at the other they were drawn out to a long capillary bent at right angles to the tube. To fill a tube with the liquid, it was heated, the end of the capillary dipped into the liquid, and the tube was allowed to cool. The liquid was then boiled off so as to fill the tube with vapour; on again cooling, the liquid completely filled the tube; if not, the operation was repeated. Finally the liquid was boiled until only the requisite amount of liquid remained, the tube was sealed at the capillary end, which was then thickened and bent in the form of a hook, the other end of the tube being also provided with a hook to facilitate suspension.

The tube containing the liquid was heated in a three-chambered air-bath of the form usually employed for a similar purpose. This air-bath was made of tinned iron, and two parallel sides of each of the three concentric chambers were provided with mica windows; behind these windows was placed a light in the line of sight. The middle chamber had four false bottoms of wire gauze to distribute the heat and each chamber was closed by an asbestos board above, perforated to admit the thermometer, which was filled with nitrogen under 20 atmospheres pressure. The heat was obtained from one of Fletcher Russell & Co.'s special high-power burners. The bulb was heated gradually until the meniscus disappeared and striations appeared in the vapour; the thermometer was then read. The bulb was next allowed to cool slowly and the temperature at which the meniscus reappeared was

noted. The heating and cooling were repeated a second time and the mean of the four observations taken.

Each liquid was subjected to at least two such experiments, one with the tube about half full of liquid and the second with the tube one-third full, so that the final result is the mean of at least eight readings. Sometimes an experiment was made with smaller quantities of liquid when satisfactory results were not obtained with the half filled tube.

Results of Experiments.—The mean of the first and second experiments is given to show how far the results are concordant.

Alcohols.

iso*Propyl Alcohol.*—Three experiments were made, namely, with the tube about one-half full, one-third full, and one-fourth full of liquid. Mean value of θ for *iso*propyl alcohol = 243·47°.

The result is probably too low, owing to the supercooling of the vapour delaying the reappearance of the meniscus.

iso*Butyl Alcohol.*—Two experiments were made giving eight observations of the temperature with the stem of the thermometer not wholly immersed in the air-bath. The mean value of θ was 279·07°.

This was not satisfactory, and two experiments were then made with the stem of the thermometer wholly immersed in the air-bath, when the mean value of θ for *iso*butyl alcohol was found to = 277·63°.

The latter was taken as correct, but it may be too low owing to supercooling delaying the reappearance of the meniscus.

sec.-*Butyl Alcohol*:—1st Experiment.—The tube, which was one-third full of the pure dry alcohol, was heated gradually in the air-bath until the meniscus disappeared and striations appeared in the va pour; the thermometer reading was taken at this point. The tube was then allowed to cool slowly and the thermometer again read when the meniscus reappeared. The heating and cooling were repeated a second time.

	Meniscus disappeared.	Meniscus reappeared.
(1)	265·3°	265·5°
(2)	265·6	265·6

2nd Experiment.—Tube about half full of the alcohol.

	Meniscus disappeared.	Meniscus reappeared.
(1)	264·8°	264·8°
(2)	265	265·1

Mean critical temperature of *sec.*-butyl alcohol = 265·19°.

iso*Amyl Alcohol* (chiefly active, but contains some inactive).—The boiling point was constant at 130·1°. Two experiments were made

with very concordant results, the mean value of θ for *iso*amyl alcohol being 309·77°.

tert.-*Amyl Alcohol.*—Two experiments were made with concordant results, the mean value of θ for *tert.*-amyl alcohol being 271·77°.

n-*Heptyl Alcohol.*—Two experiments were made; eight observations, maximum 366·5°, minimum 363·25°, the mean value of θ for *n*-heptyl alcohol being 365·3°.

n-*Octyl Alcohol.*—Two experiments were made; eight observations, maximum 387·25°, minimum 383·5°, the mean value of θ for *n*-octyl alcohol being 385·46°.

sec.-*Octyl Alcohol.*—Maximum 364·5°, minimum 363·75°, the mean value of θ being 364·12°.

Acids.

Several attempts were made to determine the critical temperature of formic acid, using very pure and carefully dried specimens, but in every case the tubes burst owing to decomposition before a critical temperature was reached. There is therefore no critical temperature for formic acid.

In each of the following cases, two experiments with eight observations were made, one with the tube one-third full, one with the tube half full.

n-*Butyric Acid.*—Maximum 355°, minimum 354·5°, the mean value of θ being 354·74°.

iso*Butyric Acid.*—Maximum 336·5°, minimum 336°, the mean value of θ being 336·25°.

n-*Valeric Acid.*—(i) The tube half full of liquid: maximum 378°, minimum 377·5°. (ii) The tube one-third full of liquid gave a higher result, maximum 380°, minimum 379·5°, the mean value of θ being 378·87°.

iso*Valeric Acid.*—Maximum 361°, minimum 360·5°, the mean value of θ being 360·68°.

Esters.

Two experiments were made in each case; eight observations.

Ethyl iso*Valerate.*—Maximum 315·5°, minimum 314·5°, mean value of θ being 314·87°.

iso*Amyl Acetate.*—Maximum 327°, minimum 325·5°, mean value of θ being 326·18°.

Propyl iso*Valerate.*—Maximum 336°, minimum 335·5°, mean value of θ being 335·93°.

iso*Butyl* iso*Butyrate.*—Maximum 329°, minimum 328·5°, mean value of θ being 328·74°.

iso*Butyl Butyrate.*—Maximum 338·5°, minimum 338°, mean value of θ being 338·25°.

iso*Amyl Propionate.*—Maximum 338·5°, minimum 338°, mean value of θ being 338·24°.

iso*Butyl* iso*Valerate.*—Maximum 348·5°, minimum 348°, mean value of θ being 348·25°.

iso*Amyl Butyrate* (tube half full).—Maximum 347°, minimum 346°; tube one-third full gave a lower result, maximum 345·5°, minimum 344·5°, mean value of θ being 345·68°.

Ethyl Caprylate.—Maximum 386·5°, minimum 384·5°, mean value of θ being 385·56°.

Ethyl Nonylate.—(i) Tube half full of liquid: maximum 402°, minimum 402°; (ii) tube one-third full gave a lower result, maximum 400°, minimum 399·5°, mean value of θ being 400·81°.

Aromatic Hydrocarbons.

Two experiments were made in each case; eight observations.

	Maximum.	Minimum.	Mean value of θ.
o-Xylene	364°	362°	362·95°
m-Xylene	349·5	348·5	349
p-Xylene	349	348	348·5
Mesitylene	371	369·75	370·5
Cymene.....	387	384	385·15

The values of $\frac{ML}{\Theta}$ can now be calculated from the latent heat and critical temperature determinations.

Alcohols (Trans., 1903, **83**, 991).

B. p.		θ.	L.	$\frac{ML}{\Theta}$.
82·85°	*iso*Propyl	243·47	161·1	18·71
108·1	*iso*Butyl.....	277·63	138·4	18·59
100·0	*sec.*-Butyl	265·19	136·2	18·72
130·1	*iso*Amyl (active) ...	309·77	124·7	18·83
101·8	*tert.*-Amyl	271·77	115·65*	18·68
176·0	*n*-Heptyl	365·3	105·0	19·08
195·0	*n*-Octyl	385·46	97·46	19·24
179·5	*sec.*-Octyl	364·12	94·48	19·27

* Trans., 1905, **87**, 269.

The *iso*propyl and *iso*butyl alcohol numbers for critical temperature are probably nearly a degree too low.

Acids (Trans., 1903, **83**, 992).

B. p.		θ.	L.	$\frac{ML}{\Theta}$.
	Formic	Decomposes below its critical temperature.		
	Acetic	321·5 (Pawlewski)	97·05	9·78
	Propionic	339·9 ,,	128·93	15·55
164°	*n*-Butyric	354·75	113·96	15·9
153	*iso*Butyric	336·25	111·5	16·1
185	*n*-Valeric	378·87	103·1	16·13
175	*iso*Valeric	360·68	101·03	16·26

Esters (Trans., 1903, **83**, 994).

B. p.			θ.	L.	$\frac{ML}{\Theta}$.
134·3°	C_7	Ethyl *iso*valerate	314·87	67·84	15·00
143·0		*iso*Amyl acetate	326·18	69·00	14·97
158·4	C_8	Propyl *iso*valerate	335·93	64·37*	15·22
148·4		*iso*Butyl *iso*butyrate	328·74	63·4	15·17
157·0		*iso*Butyl butyrate	338·25	64·59	15·21
160·5		*iso*Amyl propionate	338·24	65·31	15·38
170·0	C_9	*iso*Butyl *iso*valerate	348·25	60·41	15·36
179·6		*iso*Amyl butyrate	345·68	61·79	15·78
207·0	C_{10}	Ethyl caprylate	385·56	60·46	15·79
225·0	C_{11}	Ethyl nonylate	400·81	58·08	16·03

* Trans., 1905, **87**, 269.

In consequence of the higher values of $\frac{ML}{\Theta}$ thus obtained for the denser esters, the determinations of the critical temperature of some and of the latent heat of the whole of the esters were repeated with carefully repurified specimens, dried over phosphoric oxide and distilled. The results remained the same, and the values are therefore considered correct except in the case of ethyl nonylate, of which the quantity employed was smaller, and it may have been less perfectly purified and dried. The critical point may be a little too low. The lowest reading was 399·5° repeated three times and the highest 402° repeated four times out of eight readings.

Aromatic Hydrocarbons.

B. p.		θ.	L.	$\frac{ML}{\Theta}$.
144·0°	*o* Xylene	362·95	82·47	13·74
139·0	*m*-Xylene	349·0	81·34	13·86
138·5	*p*-Xylene	348·5	80·98	13·81
165·4	Mesitylene	370·5	74·42	13·87
177·0	Cymene	385·15	67·64	13·77

Cumene was not sufficiently pure.

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THE UNIVERSITY OF LIVERPOOL.