LXXVIII.—*Correction of the Boiling Points of Liquids from Observed to Normal Pressure.*

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IN papers published jointly with Dr. Ramsay (*Brit. Assoc. Rep.*, 1885, 928; *Phil. Mag.*, 1885, [v], 20, 515), it was pointed out that (1) the values of $dp/dt.T$ (where dp/dt is the rate of increase of vapour pressure per unit rise of temperature, and T is the boiling point on the absolute scale) are approximately the same for different substances when compared at the same pressure, but that (2) the differences are real and are not due to errors of experiment, for they preserve the same relative value whatever the pressure at which the comparison is made, at any rate within the limits of the actual experiments. It was further pointed out that for two closely-related substances, the boiling points on the absolute scale bear a constant ratio to each other at all pressures, and that for other substances (*Phil. Mag.*, 1886, [v], 21, 33) the relation between the boiling points may be expressed by an equation which can be written thus:

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + C(T_B' - T_B),$$

where T_A' and T_B' are the boiling points of the two substances on the absolute scale at a pressure, p' , T_A and T_B the boiling points at a pressure, p , and c is a very small constant.

In the light of these generalisations, Crafts (*Ber.*, 1887, 20, 709) devised a convenient method for the correction of the boiling points of substances from observed to normal pressure.

Crafts gives the boiling points (absolute temperatures), the values of $\Delta t/\Delta p$ between 720 and 770 mm. pressure, and the quotients $\frac{\Delta t}{\Delta p} \cdot \frac{1}{T} = H$ for 25 substances, and points out that when the boiling point of any liquid is to be corrected, the constant, H , for that compound in the table most closely related to it is to be taken and is to be multiplied by the approximate absolute boiling point of the substance under examination, in order to find the value of $\Delta t/\Delta p$ for a barometric variation of the 50 mm. between 720 and 770 mm

Nernst (*Theoretische Chemie*, 1893, p. 55) reproduces this table, but divides the constants, H , by 50, so as to give the mean variation of temperature per mm. change of pressure between the same limits.

There are a few misprints in Crafts' table which reappear in the modified table given by Nernst, and since 1887 the vapour pressures of a considerable number of additional compounds have been accurately determined; it may therefore be useful to give a revised and enlarged table for reference.

Instead of calculating the mean value of the constant for a range of pressure between 720 and 770 mm., I have thought it better to give the actual value of $\frac{dt}{dp} \cdot \frac{1}{T} = C$ at 760 mm., and therefore the constants in this paper differ slightly from those in Nernst's table; in most cases, the new values are lower by 2 in the last place, and this may be taken as the average difference between the value of C at 760 mm. and the mean value between 720 and 770 mm.

In calculating the value of dp/dt at the boiling point, Biot's formula, $\log p = a + ba^t + c\beta^t$, was employed when the constants for this formula had already been ascertained; in other cases, for which the vapour pressures have been determined through a sufficient range of temperature, constants for the simpler formula, $\log p = a + ba^t$, were calculated from the vapour pressures at three temperatures 20° , 30° , or 40° apart, the middle temperature being near the boiling point under normal pressure. This method was adopted, for example, in the case of the 29 esters of the methyl formate series for which accurate data are available.

For the elementary gases, and for carbon monoxide and methane, the vapour pressure data are not sufficient for this method to be employed, and the formula, $\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + c(T_B' - T_B)$, was made use of, benzene being taken as the standard substance. The constant, c , was first calculated from the boiling point and critical temperature of the gas and the boiling point of benzene under normal pressure and at a pressure equal to the critical pressure of the gas, the assumption being made that Biot's formula might be employed for benzene for some little distance above its actual critical point. It is probable that the boiling points and critical constants of the gases are less accurately known than the vapour pressures of the majority of substances included in the tables that follow, and as the method of calculation of dp/dt is also less direct, the values of C are probably less accurate. The constants determined in this way are marked with an asterisk.

$$\text{Values of } C = \frac{dt}{dp} \cdot \frac{1}{T} \text{ at 760 mm.}$$

Name of substance.	Boiling point (abs. temp.).	dp/dt	C .	Observer.
Oxygen.....*	90.3°	75.9	0.000146	Olszewski.
Nitrogen.....*	77.5	89.0	0.000145	Baly.
Argon.....*	86.9	83.2	0.000138	Ramsay and Travers.
Krypton.....*	121.3	61.8	0.000133	" "
Xenon.....*	163.9	45.9	0.000133	" "
Chlorine.....	239.4	33.2	0.000126	Knietzsch.
Bromine.....	331.75	25.2	0.000120	Ramsay and Young
Iodine.....	458.3	18.75	0.000116	" "
Mercury.....	629.8	13.4	0.000118	Young.
Sulphur.....	721.4	12.2	0.000114	Regnault.
Carbon monoxide...*	83.0	81.3	0.000148	Olszewski.
Sulphur dioxide.....	262.9	33.7	0.000113	Regnault.
Ammonia.....	240.1	37.7	0.000110	"
Carbon disulphide ...	319.25	24.7	0.000127	"
Boron trichloride.....	291.25	26.8	0.000128	"
Phosphorus trichloride.....	346.85	23.45	0.000123	"
Silicon tetrachloride.....	329.9	24.0	0.000126	"
Stannic chloride.....	387.1	21.4	0.000121	"
Methyl chloride.....	249.35	31.9	0.000126	"
Chloroform.....	333.2	25.2	0.000119	"
Carbon tetrachloride.....	349.75	23.25	0.000123	Young.
Methane.....*	109.0	68.2	0.000135	Olszewski.
<i>n</i> -Pentane.....	309.3	25.8	0.000125	Young.
<i>n</i> -Hexane.....	341.95	23.9	0.000122	"
<i>n</i> -Heptane.....	371.4	22.3	0.000121	"
<i>n</i> -Octane.....	398.8	21.1	0.000119	"
<i>iso</i> Pentane.....	300.95	26.2	0.000127	"
Diisopropyl.....	331.1	24.3	0.000124	Young and Fortey.
Diisobutyl.....	382.1	20.9	0.000125	" "
<i>cyclo</i> Hexane.....	353.9	22.7	0.000124	" "
Benzene.....	353.2	23.3	0.000122	Young.
Toluene.....	383.7	21.8	0.000120	Young and Fortey.
Naphthalene.....	491	17.1	0.000119	Crafts.
Anthracene.....	616	15.0	0.000108	"
<i>m</i> -Xylene.....	412	21.1	0.000115	"
Diphenylmethane ...	538	15.1	0.000123	"
Triphenylmethane ...	626	14.8	0.000108	"
Fluorobenzene.....	358.2	23.3	0.000120	Young.
Chlorobenzene.....	405.0	20.5	0.000120	"
Bromobenzene.....	429.0	19.3	0.000120	"
Iodobenzene.....	461.45	18.0	0.000120	"
Bromonaphthalene ...	553.45	15.75	0.000115	Ramsay and Young.
Ethylene dibromide.....	405	20.8	0.000119	Crafts.
Methyl ether.....	249.4	32.0	0.000125	Regnault.
Ethyl ether.....	307.6	26.9	0.000121	Ramsay and Young.
Acetone.....	330	26.4	0.000115	Crafts.

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Values of $C = \frac{dt}{dp} \cdot \frac{1}{T}$ at 760 mm. (continued).

Name of substance.	Boiling point (abs. temp.).	dp/dt .	C .	Observer.
Benzophenone	578·8°	15·8	0·000109	Crafts.
Dibenzylketone	603·55	15·2	0·000109	Young.
Anthraquinone	650	13·6	0·000113	Crafts.
Aniline	457·4	19·6	0·000112	Ramsay and Young.
Quinoline	510·5	17·0	0·000115	Young.
Methyl formate	304·9	28·8	0·000114	Young and Thomas.
Ethyl formate	327·3	26·6	0·000115	" "
Methyl acetate	330·1	26·8	0·000113	" "
Propyl formate	353·9	24·5	0·000115	" "
Ethyl acetate	350·15	25·1	0·000114	" "
Methyl propionate ...	352·7	24·9	0·000114	" "
isoButyl formate....	370·85	23·45	0·000115	Schumann.
Propyl acetate	374·55	23·5	0·000114	Young and Thomas.
Ethyl propionate	372·0	23·7	0·000113	" "
Methyl butyrate	375·75	23·3	0·000114	" "
Methyl isobutyrate...	365·3	23·8	0·000115	" "
Amyl formate	396·25	21·8	0·000115	Schumann.
isoButyl acetate	389·2	22·5	0·000114	" "
Propyl propionate ...	395·15	22·3	0·000114	" "
Ethyl butyrate	392·9	22·3	0·000114	" "
Ethyl isobutyrate ...	383·1	22·5	0·000116	" "
Methyl valerate	389·7	22·4	0·000114	" "
isoButyl propionate	409·8	21·4	0·000114	" "
Propyl butyrate	415·7	20·9	0·000115	" "
Propyl isobutyrate ...	406·9	21·8	0·000113	" "
isoPropyl isobutyrate	393·75	22·0	0·000115	Young and Fortey.
Ethyl valerate	407·3	21·4	0·000115	Schumann.
Amyl propionate.....	433·2	20·4	0·000113	" "
isoButyl butyrate ...	429·9	20·5	0·000113	" "
isoButyl isobutyrate	419·6	20·6	0·000116	" "
Propyl valerate	428·9	20·5	0·000114	" "
Amyl butyrate.....	451·6	19·5	0·000113	" "
Amyl isobutyrate ...	441·8	19·6	0·000115	" "
isoButyl valerate.....	441·7	19·9	0·000114	" "
Methyl alcohol.....	337·9	29·6	0·000100	Ramsay and Young.
Ethyl alcohol	351·3	30·35	0·000094	" "
Propyl alcohol.....	370·4	28·8	0·000094	" "
Amyl alcohol	403	25·3	0·000098	Crafts.
Phenol	456	20·5	0·000107	" "
Acetic acid	391·5	23·9	0·000107	Young.
Phthalic anhydride...	559	16·0	0·000112	Crafts.
Sulphobenzide	652	15·2	0·000101	" "
Water	373·0	27·2	0·000099	Regnault.

It will be seen that the values of C ($\times 10^6$) vary from about 145 in the case of oxygen, nitrogen, and carbon monoxide to 99 for water and 94 or ethyl and propyl alcohols.

The following relations are clearly observable :

1. In most groups of similar substances the greater the molecular complexity the lower is the constant. This is well seen in the case of the normal paraffins ; of benzene, naphthalene, and anthracene ; of methyl and ethyl ether, and of acetone and benzophenone or dibenzyl ketone.

2. Rise of molecular weight without increased complexity either causes a similar change or has no influence ; thus, for the halogens C diminishes from chlorine to iodine ; but, on the other hand, it has the same value for the four halogen derivatives of benzene.

3. Comparing isomeric substances, it is seen that C is almost always lower for normal than for *iso*-compounds, and lower for these than for compounds that contain two *iso*-groups.

4. By replacement of hydrogen by a halogen, the constant is lowered ; thus benzene, 122, chlorobenzene 120 ; naphthalene 119, bromonaphthalene 115 ; ethane, above 125, ethylene dibromide, 119.

5. When there is association of molecules in the liquid state, the value is low ; this is the case with water, the alcohols, phenol, and acetic acid, all of which contain a hydroxyl group.

6. In the case of organic hydroxyl compounds, the influence of the hydroxyl group diminishes as the complexity of the organic radicle increases, and thus the depression of the constant diminishes, but, on the other hand, the constant tends to fall as the complexity of the molecule increases. There are thus two opposing influences, and in the group of alcohols the constant shows considerable irregularity.

In the case of the esters, there is evidence of some molecular association in the liquid state and at the critical point, and we find similar opposing influences, with the result that the variation in the constant is very small ; indeed, for the whole 29 esters the extreme values are 113 and 116. Still, if we confine our attention to the higher esters containing, say, 5 or more carbon atoms, (1) the influence of molecular complexity, and (2) of constitution, is, with few exceptions, to be observed, and in the table on p. 782 the results are summarised to bring out this point :

In order to correct a boiling point from observed to normal pressure, Δ_t is to be added, where

$$\Delta_t = (760 - p)(273 + t).C.$$

The constant C is to be ascertained from the preceding tables, taking account, if necessary, of the relations (1) to (6) ; p is the observed pressure and t is the boiling point as observed or, better, roughly corrected.

In a series of papers (*Phil. Mag.*, 1892, [v], 34, 503 ; *Trans.*, 1893, 63, 1254 ; *Phil. Mag.*, 1894, [v], 37, 1 ; *ibid.*, 1900, [v], 50, 291), I

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Formula of ester.	Normal.		One <i>iso</i> -group.		Two <i>iso</i> -groups.	
	<i>C.</i>	Mean.	<i>C.</i>	Mean.	<i>C.</i>	Mean.
C ₂ H ₄ O ₂	0·0001139	0·0001139	—	—	—	—
C ₃ H ₆ O ₂	0·0001149 0·0001130 0·0001151	0·0001140	—	—	—	—
C ₄ H ₈ O ₂	0·0001138 0·0001136 0·0001142		—	—	—	—
C ₅ H ₁₀ O ₂	0·0001134 0·0001136		0·0001150 0·0001150 0·0001155	0·0001150	—	—
C ₆ H ₁₂ O ₂	0·0001137 0·0001141	0·0001139	0·0001139 0·0001158 0·0001143		—	—
C ₇ H ₁₄ O ₂	0·0001148		0·0001140 0·0001147 0·0001127	0·0001138	0·0001155	0·0001155
C ₈ H ₁₆ O ₂	—	—	0·0001129 0·0001135 0·0001136		0·0001156	0·0001156
C ₉ H ₁₈ O ₂	—	—	0·0001134	0·0001134	0·0001152 0·0001138	0·0001145
Mean...	0·0001140		0·0001142		0·0001150	

have shown that, excluding compounds which contain a hydroxyl group, the ratio, $\frac{D_c}{D'_c}$, of the actual to the theoretical density for a perfect gas at the critical point is approximately constant, the mean value being about 3·76, but that the deviations are real ones and are related to the molecular weight and constitution of the substances.

I have also shown that Cailletet and Mathias' law of the "diameter" is not in most cases absolutely true, although very nearly so, and that the relation of the mean density to the temperature should be expressed by the formula $D_t = D_0 + at + \beta t^2$, where α is always negative, and β changes from a very small positive value, through zero, to a very small negative value as the ratio $\frac{D_c}{D'_c}$ increases.

Again taking the approximate formula $D_t = D_0 + at$, originally given by Cailletet and Mathias, it has been proved independently by Mathias and myself that, if the generalisations of Van der Waals were strictly true, $\frac{\alpha T_c}{D_c}$ should be a constant for all substances; but I have shown that there are real though not large deviations in this case also, the value of $\frac{\alpha T_c}{D_c}$ rising in general as $\frac{D_c}{D'_c}$ increases.

It is of interest to observe that, as a rule, $C \left(= \frac{d \, t l}{d p \, T} \right)$ at normal pressure diminishes as $\frac{D_c}{D_c'}$ rises.

So far, then, as the 26 substances which I have myself examined are concerned, there is clearly a connection between the four constants $\frac{D_c}{D_c'}$, β , $\frac{\alpha T_c}{D_c}$, and C .

The critical densities of the gaseous elements are not known with sufficient precision to allow of any very definite statement being made regarding the value of $\frac{D_c}{D_c'}$, but it is interesting to note that D. Berthelot points out that for carbon dioxide this constant is lower (3.6) than for any of the substances I have investigated, whilst for oxygen and nitrogen it appears to be about 3.5.

The constant $C \, (\times 10^6)$ for the two last named gases is about 145, and if a diagram is constructed to show the relation between C and $\frac{D_c}{D_c'}$ and these values, $C = 145$ and $\frac{D_c}{D_c'} = 3.5$ are mapped with the others, including also those of ethyl and propyl alcohols, the connection between C and $\frac{D_c}{D_c'}$ becomes quite evident, the former falling as the latter rises. Methyl alcohol and acetic acid have low, but not proportionately low, values of the constant C .

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