Some Thermodynamical Relations. - Part V

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Substance.	Pressures from which n was calculated.	Value of n .
Carbon disulphide . . .	50 and 5000	1·147
Ethyl bromide . . .	50 and 5000	1·316
Ethyl chloride . . .	50 and 5000	1·243
Carbon tetrachloride . .	50 and 5000	1·326
Bromobenzene . . .	50 and 800	1·475
Chlorobenzene . . .	100 and 700	1·480
Chloroform . . .	200 and 5000	1·376
Ethylene . . .	10 and 400	1·235
Sulphur . . .	300 and 3000	1·251
Bromo-naphthalene . .	150 and 800	1·196
Methyl salicylate . . .	50 and 800	1·517
Aniline . . .	50 and 800	1·218
Methyl alcohol . . .	50 and 5000	1·395

It was found impossible to obtain a constant value for n with dissociating substances when different pressures were employed.

The whole subject of vapour-pressure is one that cannot well be considered on its own merits, for they must evidently be intimately related to other physical properties; and although we have already accumulated data for alcohol and ether bearing on this subject, we prefer to reserve a general consideration of the question until an investigation, as regards the thermal behaviour of other bodies, on which we are at present engaged, shall have been finished.

X. *Some Thermodynamical Relations.*—PART V.

By WILLIAM RAMSAY, *Ph.D.*, and SYDNEY YOUNG, *D.Sc.**

IN the first two of the series of papers on "Some Thermodynamical Relations," published in the previous volume of the 'Proceedings' (vol. vii.), it was shown by one of us that the ratio of the absolute temperatures of nearly related bodies, such as chlorobenzene and bromobenzene, or ethyl chloride and ethyl bromide, is constant for equal vapour-pressures; and that a relation exists between the ratios of the absolute temperatures of all bodies which may be expressed

* Read May 22, 1886.

by the equation

$$R' = R + c(t' - t),$$

where R is the ratio of the absolute temperatures of the two bodies corresponding to any vapour-pressure, the same for both ; R' is the ratio at any other vapour-pressure, again the same for both ; c is a constant which may be 0 or a small + or - number ; and t' and t are the temperatures of one of the two bodies corresponding to the two vapour-pressures.

The determination of the vapour-pressures of a large series of compound ethers by Schumann (Wiedemann's *Annalen*, 1881, p. 40) affords an opportunity of studying the relations of a great number of bodies of the same type ; and it appears that in this case also the ratio of the absolute temperatures of any two of the ethers is a constant at all pressures. The following table shows the ratios of the absolute temperatures of all the ethers

Ratios of Absolute Temperatures of Ethers to those of Ethyl Acetate at definite Pressures.

Ether.	Pressure.			Mean.
	1300 millim.	760 millim.	200 millim.	
Methyl formate.....	·8715	·8720	·8706	·8714
Ethyl formate.....	·9344	·9352	·9323	·9340
Propyl formate.....	1·0109	1·0111	1·0115	1·0112
Isobutyl formate	1·0585	1·0594	1·0573	1·0584
Amyl formate	1·1345	1·1320	1·1329	1·1331
Methyl acetate	·9420	·9440	·9431	·9430
Propyl acetate	1·0678	1·0677	1·0690	1·0682
Isobutyl acetate.....	1·1122	1·1120	1·1120	1·1121
Methyl propionate	1·0073	1·0080	1·0073	1·0075
Ethyl propionate	1·0615	1·0605	1·0614	1·0611
Propyl propionate	1·1290	1·1288	1·1291	1·1290
Isobutyl propionate.....	1·1704	1·1705	1·1705	1·1705
Amyl propionate	1·2366	1·2374	1·2401	1·2380
Methyl butyrate	1·0724	1·0720	1·0716	1·0720
Ethyl butyrate	1·1220	1·1223	1·1202	1·1215
Propyl butyrate	1·1889	1·1874	1·1902	1·1888
Isobutyl butyrate	1·2279	1·2279	1·2278	1·2279
Amyl butyrate	1·2905	1·2899	1·2901	1·2902
Methyl isobutyrate	1·0444	1·0434	1·0433	1·0437
Ethyl isobutyrate.....	1·0953	1·0943	1·0935	1·0944
Propyl isobutyrate	1·1604	1·1623	1·1609	1·1612
Isobutyl isobutyrate.....	1·2001	1·1985	1·1985	1·1990
Amyl isobutyrate	1·2644	1·2619	1·2637	1·2633
Methyl valerate	1·1135	1·1131	1·1139	1·1135
Ethyl valerate	1·1642	1·1634	1·1619	1·1632
Propyl valerate.....	1·2257	1·2251	1·2265	1·2258
Isobutyl valerate	1·2635	1·2617	1·2634	1·2629

to those of ethyl acetate at pressures of 200, 760, and 1300 millims. (The boiling-points at these pressures are given by Schumann.) It will be seen that in every case the ratio is very nearly constant at each pressure; and the deviations from constancy may well be due to the great difficulty of obtaining perfectly pure specimens, evidenced by the fact that only one ether boiled with perfect constancy, the rise of temperature during distillation amounting in one case to $0^{\circ}\cdot7$, while the average rise was $0^{\circ}\cdot37$. The absolute temperatures of ethyl acetate corresponding to 1300, 760, and 200 millim. are $367^{\circ}\cdot3$, $350^{\circ}\cdot1$, and $314^{\circ}\cdot4$.

Taking the mean ratio for each ether, and the temperatures of ethyl acetate at the three pressures as correct, the boiling-point of the ethers were recalculated; and the following table contains these values, together with the observed temperatures and the differences between the observed and calculated temperatures:—

Absolute Temperatures.

Ether.	Observed.			Calculated.			Differences.		
	1300 mm.	760 mm.	200 mm.	1300 mm.	760 mm.	200 mm.	1300 mm.	760 mm.	200 mm.
Methyl formate.....	320.1	305.3	273.7	320.1	305.1	274.0	0	-0.2	+0.3
Ethyl formate	343.2	327.4	293.1	343.1	327.0	293.6	-0.1	-0.4	+0.5
Propyl formate	371.3	354.0	318.0	371.4	354.0	317.9	+0.1	0	-0.1
Isobutyl formate ...	388.8	370.9	332.4	388.7	370.5	332.8	-0.1	-0.4	+0.4
Amyl formate	416.7	396.3	356.2	416.2	396.7	356.2	-0.5	+0.4	0
Methyl acetate	346.0	330.5	296.5	346.4	330.0	296.5	+0.4	-0.5	0
Propyl acetate	392.2	373.8	336.1	392.3	374.0	335.8	+0.1	+0.2	-0.3
Isobutyl acetate ...	408.5	389.3	349.6	408.5	389.3	349.6	0	0	0
Methyl propionate..	370.0	352.9	316.7	370.1	352.7	316.8	+0.1	-0.2	+0.1
Ethyl propionate ...	389.9	371.3	333.7	389.7	371.5	333.6	-0.2	+0.2	-0.1
Propyl propionate...	414.7	395.2	355.0	414.7	395.3	355.0	0	+0.1	0
Isobutyl propionate	429.9	409.8	368.0	429.9	409.8	368.0	0	0	0
Amyl propionate ...	454.2	433.2	389.9	454.7	433.4	389.2	+0.5	+0.2	-0.7
Methyl butyrate ...	393.9	375.3	336.9	393.7	375.3	337.0	-0.2	0	+0.1
Ethyl butyrate	412.1	392.9	352.2	411.9	392.6	352.6	-0.2	-0.3	+0.4
Propyl butyrate ...	436.7	415.7	374.2	436.6	416.2	373.8	-0.1	+0.5	-0.4
Isobutyl butyrate ...	451.0	429.9	386.0	451.0	429.9	386.0	0	0	0
Amyl butyrate	474.0	451.6	405.6	473.9	451.7	405.6	-0.1	+0.1	0
Methyl isobutyrate..	383.6	365.3	328.0	383.4	365.4	328.1	-0.2	+0.1	+0.1
Ethyl isobutyrate ...	402.3	383.1	344.1	402.0	383.2	344.1	-0.3	+0.1	0
Propyl isobutyrate..	426.2	406.9	365.0	426.5	406.5	365.1	+0.3	-0.4	+0.1
Isobutyl isobutyrate	440.8	419.6	376.8	440.4	419.8	377.0	-0.4	+0.2	+0.2
Amyl isobutyrate ...	464.4	441.8	397.3	464.0	442.3	397.2	-0.4	+0.5	-0.1
Methyl valerate.....	409.0	389.7	350.2	409.0	389.8	350.1	0	+0.1	-0.1
Ethyl valerate	427.6	407.3	365.3	427.2	407.2	365.7	-0.4	-0.1	+0.4
Propyl valerate.....	450.2	428.9	385.6	450.2	429.2	385.4	0	+0.3	-0.2
Isobutyl valerate ...	464.1	441.7	397.2	463.9	442.1	397.1	0.2	+0.4	-0.1

It will be noticed that the greatest difference between the observed and recalculated temperatures is $0^{\circ}\cdot 7$, which is probably within the limits of experimental error, for the reason already stated. If this is so, the equation $\frac{t_2'}{t_1'} = \frac{t_2}{t_1}$ holds good for this series of ethers, where t_2' and t_2 are the absolute temperatures of any one of the ethers corresponding to two vapour-pressures, and t_1' and t_1 the absolute temperatures of any other ether at the same pressures. If the ethers are compared with some other substance, such as water, the equation

$$\frac{t_1'}{T'} = \frac{t_1}{T} + c(T' - T)$$

must be employed, where t_1' and t_1 are the absolute temperatures of the ether, and T' and T those of water at any two pressures. If the left side of this equation be multiplied by $\frac{t_2'}{t_1'}$ and the right by $\frac{t_2}{t_1}$, $\frac{t_2'}{t_1'}$ being equal to $\frac{t_2}{t_1}$, the equation becomes

$$\begin{aligned} \frac{t_2'}{T'} &= \frac{t_2}{t_1} \left\{ \frac{t_1}{T} + c(T' - T) \right\} \\ &= \frac{t_2}{T} + c \frac{t_2}{t_1} (T' - T). \end{aligned}$$

That is to say, if the members of this series of ethers be compared with water, both the ratios at any given pressure, corresponding to t_1 , t_2 , &c. and the constant c vary directly as the boiling-points (absolute) of the ethers at that pressure.

Taking the boiling-point of ethyl acetate at the normal pressure to be correct, and the ratio of the absolute temperature of ethyl acetate to that of water at that pressure therefore to be $\frac{350\cdot 1}{373\cdot 0} = 0\cdot 9386$, and the value of c to be $0\cdot 000387$, the ratio of the absolute temperature of ethyl acetate to that of water at any other pressure is given by the equation

$$\frac{t'}{T'} = 0\cdot 9386 + 0\cdot 000387 (T' - 373),$$

where t' is the absolute temperature of ethyl acetate, and T' that of water.

The calculated and observed temperatures are :—

Pressure.	Temperature.	
	Observed.	Calculated.
1300	367·3	367·2
200	314·4	314·4

For any other ether in the series the equation is

$$\frac{t'}{T'} = \frac{t}{350\cdot1} \{0\cdot9386 + 0\cdot000387 (T' - 373)\},$$

where t is the boiling-point of the ether at constant pressure.

For pressures of 1300 and 200 millim. respectively the equation becomes simply

$$t' = 1\cdot0488t$$

and

$$t' = 0\cdot89795t.$$

It appears therefore that by determining simply the boiling-point of an ether belonging to this type, and knowing the vapour-pressures of water (or of one of the other ethers), it is possible to calculate the temperatures corresponding to any other pressure, at any rate between the limits of 200 and 1300 millim.