XLIV. Note on the effect of the replacement of oxygen by sulphur on the boiling- and melting-points of compounds

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Temperature Cent.	Specific Gravity.
25°	·831
30	·8306
35	·828
40	·826
45	·8758
50	·8753
55	·8717

We are now arranging a piece of apparatus which will give, not the absolute value of the specific gravity, but with great accuracy relative rates of the change of specific gravity with temperature *. We shall make experiments of the same kind upon other animal oils.

XLIV. *Note on the Effect of the Replacement of Oxygen by Sulphur on the Boiling- and Melting-points of Compounds.*
By Miss A. G. EARP †.

IN various papers published in the Philosophical Magazine ‡ Carnelley has called attention to the effect produced on the boiling-point and melting-point of compounds by replacing one element in the compound by another belonging to the same group. He gives numerous examples (mostly organic compounds) to show that in the case of the halogen compounds, when one halogen is replaced by another of a higher atomic weight, both the boiling- and melting-point are correspondingly raised.

As a further instance of the same kind of thing he gives the following series of the ethyl carbonates and sulpho-carbonates to show that the boiling-point is raised in proportion to the amount of sulphur introduced in the place of oxygen. He also points out that the same series shows that a definite effect is produced by a change in the arrangement of the molecule without any change in the number of sulphur atoms.

$\text{CO} \begin{cases} \text{O}-\text{C}_2\text{H}_5 \\ \text{O}-\text{C}_2\text{H}_5 \end{cases}$ B.P. 125°.	$\text{CO} \begin{cases} \text{SC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{cases}$ B.P. 196°.
$\text{CO} \begin{cases} \text{O}-\text{C}_2\text{H}_5 \\ \text{S}-\text{C}_2\text{H}_5 \end{cases}$ B.P. 156°.	$\text{CS} \begin{cases} \text{OC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{cases}$ B.P. 200°.
$\text{CS} \begin{cases} \text{O}-\text{C}_2\text{H}_5 \\ \text{O}-\text{C}_2\text{H}_5 \end{cases}$ B.P. 161°.	$\text{CS} \begin{cases} \text{SC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{cases}$ B.P. 240°.

* We described at the Meeting results obtained for other specimens of sperm-oil, with the new apparatus, which exhibited no discontinuity. Yet we can find no reason to doubt Mr. Knight's measurements.

† Communicated by M. M. Pattison Muir.

‡ Phil. Mag. Oct. 1879.

He does not, however, mention the way in which this effect is reversed in the cases in which the oxygen of the *hydroxyl* group is replaced by sulphur, and I therefore conclude that it escaped his notice. By examining the large number of boiling-point data given by him in his tables I have found the following rule to be perfectly general:—

The replacement of oxygen by sulphur in a compound always raises the boiling-point except in those cases in which the oxygen of the hydroxyl group is replaced by sulphur, and then the reverse effect is very marked.

In obtaining data in proof of this I have been confined of course mainly to organic compounds, and of these I have only given the simpler instances, and such of the more complicated compounds as have a known structural formula. The reason for this is obvious, since Kopp has shown that the boiling-point of isomeric hydrocarbons is not the same, showing that a mere rearrangement of the atoms in a molecule is sufficient to affect the boiling-point without any change in number or kind. The fact is further exemplified in the series of ethyl-carbonates given above.

In the following list of compounds containing hydroxyl and their sulphur analogues, it will be seen that the replacement of the OH by the SH group always *lowers* the boiling-point, and that in the case of bodies of low molecular weight the difference is considerable, but decreases as we ascend a homologous series*.

			Diff.
H ₂ S.....	-61.8	H ₂ O	100
CH ₃ SH	21	CH ₃ OH	67
C ₂ H ₅ SH	36.2	C ₂ H ₅ OH	78.4
(OH) ₂ SH	146	(CH ₂ OH) ₂	197
CH ₂ OHCH ₂ SH	90	CH ₂ CHCH ₂ OH	96
CH ₂ CH ₂ CH ₂ SH	67	CH ₂ CH ₂ CH ₂ OH	97
(CH ₂) ₂ CHSH	57	(CH ₂) ₂ CHOH	83
(CH ₂) ₃ CHCH ₂ SH	88	(CH ₂) ₃ CHCH ₂ OH	108
CH ₃ CH ₂ CHSHCH ₃	84	CH ₃ CH ₂ CHOHCH ₃	99
CH(CH ₂) ₂ CH ₂ CH ₂ SH	120	CH(CH ₂) ₂ CH ₂ CH ₂ OH	131.5
CCl ₂ CHOHSH	123	CCl ₂ CHOH	149
C ₆ H ₅ SH	172	C ₆ H ₅ OH	180
C ₆ H ₄ (SH) ₂	243	C ₆ H ₄ (OH) ₂	270
CH ₂ (CH ₂) ₂ CH ₂ SH	145	CH ₂ (CH ₂) ₂ CH ₂ OH	157
C ₆ H ₅ CH ₂ SH	194	C ₆ H ₅ CH ₂ OH	205
C ₆ H ₄ CH ₂ SH (α)	188	C ₆ H ₄ CH ₂ OH (α)	188
(β)	188	(β)	201
(γ)	188	(γ)	198
CH ₃ COSH	93	CH ₃ COOH	117
C ₆ H ₅ COSH (α)	216	C ₆ H ₅ COOH (α)	245
† Exception:—C ₁₀ H ₇ SH (α)	285	C ₁₀ H ₇ (OH) (α)	278-80

* The only exception to the rule is that marked †, and is in the case of a body of high molecular weight and complicated constitution.

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Again, in the following list of compounds containing oxygen *not* in the condition of hydroxyl, it will be seen that the normal rule is followed.

			Diff.
CH_3CHS	205	CH_3CHO	21
$(\text{CH}_3)_2\text{S}$	200	$(\text{CH}_3)_2\text{O}$	13.8
$(\text{CH}_3)_3\text{S}$	41	$(\text{CH}_3)_2\text{CO}$	-23
$(\text{CH}_3)_2\text{CS}$	200	$(\text{CH}_3)_3\text{CO}$	91
$(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{S}$	64	$(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{O}$	11
$(\text{C}_2\text{H}_5)_3\text{S}$	92	$(\text{C}_2\text{H}_5)_3\text{O}$	35
$\text{CH}(\text{CH}_3)_2\text{CH}_2\text{CHS}$	114	$\text{CH}(\text{CH}_3)_2\text{CH}_2\text{CHO}$	85
$(\text{C}_2\text{H}_5)_2\text{CS}$	240	$(\text{C}_2\text{H}_5)_3\text{CO}$	125
EtSCH_2SEt	184	EtOCH_2OEt	88
$(\text{CH}_2\text{CHCH}_2)_2\text{S}$	140	$(\text{CH}_2\text{CHCH}_2)_2\text{O}$	82
$(\text{CH}_2\text{CHCH}_2)_2\text{S}_2$	188	$(\text{CH}_2\text{CHCH}_2)_2\text{O}_3$	171
$(\text{Pr})_2\text{S}(\alpha)$	130	$(\text{Pr})_2\text{O}(\alpha)$	82
" (β)	120	" (β)	60
$(\text{EtSOCH}_2)_2$	210	$(\text{EtOCH}_2)_2$	123
$\text{C}_6\text{H}_5\text{SC}_2\text{H}_5$	204	$\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$	172
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$	182	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{O}$	140
$\text{C}_6\text{H}_5\text{CH}_2\text{SEt}$	215	$\text{C}_6\text{H}_5\text{CH}_2\text{OEt}$	185
$(\text{C}_5\text{H}_{11})_2\text{S}(\text{Iso})$	250	$(\text{C}_5\text{H}_{11})_2\text{O}(\text{Iso})$	175
$(\text{C}_6\text{H}_5)_2\text{S}$	332	$(\text{C}_6\text{H}_5)_2\text{O}$	278-288
$(\text{C}_6\text{H}_5)_3\text{S}$	292	$(\text{C}_6\text{H}_5)_3\text{O}$	246
$\text{CH}_3\text{COSCH}_3$	95	$\text{CH}_3\text{COOCH}_3$	56
$\text{CO}(\text{SCH}_3)_2$	169	$\text{CO}(\text{OCH}_3)_2$	90
$\text{CH}_3\text{COSC}_2\text{H}_5$	115	$\text{CH}_3\text{COOC}_2\text{H}_5$	77
$\text{CH}_3\text{COSC}_3\text{H}_7(\alpha)$	135	$\text{CH}_3\text{COOC}_3\text{H}_7(\alpha)$	102
" (β)	124	" (β)	91
$\text{C}_6\text{H}_5\text{COOCS}$	284	$\text{C}_6\text{H}_5\text{COOCO}$	276
$\text{C}_6\text{H}_5\text{COSC}_2\text{H}_5$	242	$\text{C}_6\text{H}_5\text{COOC}_2\text{H}_7$	212
CH_3SCN	132	CH_3OCN	90
CH_3NCS	119	CH_3NCO	44
$\text{OH}\cdot\text{CHCH}_2\text{NCS}$	150	$\text{CH}_3\text{CHCH}_2\text{NCO}$	82
$\text{C}_6\text{H}_7\text{SCN}(\beta)$	151	$\text{C}_6\text{H}_7\text{OCN}(\beta)$	67
$\text{OH}(\text{CH}_3)_2\text{CH}_2\text{NCS}$	162	$\text{OH}(\text{CH}_3)_2\text{CH}_2\text{NCO}$	110
$\text{C}_6\text{H}_4\text{COSCO}$	284	$\text{C}_6\text{H}_4\text{COOCO}$	276
$\text{C}_6\text{H}_5\text{NCS}$	218	$\text{C}_6\text{H}_5\text{NCO}$	163
$\text{C}_6\text{H}_5\text{CH}_2\text{NCS}$	243	$\text{C}_6\text{H}_5\text{CH}_2\text{NCO}$	175-200
$\text{CCl}_3\text{SCCl}_3$	156-160	$\text{CCl}_3\text{OCCl}_3$	(about) 100

To the above may be added the series of ethyl carbonates quoted at first, and also the following inorganic compounds:—

CS_2	42.6	CO_2	-78.2
CSCl_2	71	COCl_2	82
PSCl_3	125	POCl_3	197

By arranging the data rather differently it is easy to see that the abnormality lies entirely with the hydroxyl group. Thus, if we take any group of sulphur compounds of one type, we shall find the boiling-point increases with the molecular weight as well when the hydrogen of the SH group is replaced by a hydrocarbon radical as in any other case.

Such, for example, are the following :—

	H_2S	-61.8		H_2S	-61.8		H_2S	-61.8
	$\text{C}_2\text{H}_5\text{SH}$	21		$\text{C}_2\text{H}_5\text{SH}$	36		$\text{C}_2\text{H}_5\text{SH}$	172
A_1	$(\text{CH}_3)_2\text{S}$	41	A_2	$(\text{C}_2\text{H}_5)_2\text{S}$	92	A_3	$\text{C}_6\text{H}_5\text{SC}_2\text{H}_5$	204
	$\text{C}_2\text{H}_5 \cdot \text{CH}_3\text{S}$	64		$\text{Pr}_2\text{S}(\alpha)$	130		$(\text{C}_6\text{H}_5)_2\text{S}$	292

Taking in the same way the corresponding oxygen compounds, we find that by replacing OH by OX, where X stands for any *hydrocarbon radical*, unless *very* complex, we *lower* the boiling-point of the compound considerably, whereas when the exchange is simply between *different hydrocarbon radicals* the change is in the normal direction.

	H_2O	100°		H_2O	100°		H_2O	100°
	CH_3OH	67		$\text{C}_2\text{H}_5\text{OH}$	78.4		$(\text{C}_6\text{H}_5)\text{OH}$	180
B_1	$(\text{CH}_3)_2\text{O}$	-23	B_2	$(\text{C}_2\text{H}_5)_2\text{O}$	35	B_3	$\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$	172
	$\text{CH}_3\text{C}_2\text{H}_5\text{O}$	11		$(\text{Pr}_2)\text{O}(\alpha)$	82		$(\text{C}_6\text{H}_5)_2\text{O}$	246*

From these data it is evident that the fact that water, which has a lower molecular weight than even any of the "permanent" gases (except hydrogen) will remain liquid up to a very high temperature, is only one particular and well-marked case of the general effect of the hydroxyl group.

It has been objected by Ostwald and others that the comparison of boiling-points is unsatisfactory, inasmuch as in some cases it is possible that the vapour-pressure curves of different substances may *cross* one another at some point; and in that case, if some other than atmospheric pressure were taken as the standard, the relative position of the boiling-points would be reversed.

It is difficult to plot the vapour-pressure curves for H_2O and H_2S on the same scale, since the pressure of H_2S varies by many atmospheres; while that of H_2O varies through the same range only by a few inches, so that it has to be represented on the H_2S scale by a line following the zero. The H_2S curve is, however, perfectly normal, and shows no tendency whatever to approach the zero at any point short of infinity. Hence the objection about the crossing of the curves falls to the ground in this case. The same may be shown by comparing the curves for CO_2 and CS_2 ; only in this case, of course, the sulphur compound follows the zero line, while the other is highly inclined.

With regard to the melting-points of oxygen and sulphur compounds the same general rule holds; but exceptions are not rare, particularly in the cases of more complicated compounds, and naturally it is among these that the larger number

* In this case the destruction of OH is not sufficient to balance the effect of introducing the second carbon ring.

of melting-point data are given. In all probability the tendency to form molecular groupings and other unknown factors tend to obscure the effect on melting-points due to the change of constitution alone.

Another point which I think may be noticed with advantage from the series just given on page 461, and which, as far as I am aware, has been hitherto neglected, is the effect on the boiling-point of the *symmetry* of the molecule, unsymmetrical molecules tending to boil higher than symmetrical ones.

Consider the series A_1 , page 461. Between the first and second members of the series there is a large difference, the molecular weight being increased and the symmetry of the molecule destroyed at the same time. Between 2 and 3 of the same series, on the other hand, there is a much smaller difference; the molecular weight is increased but symmetry is restored, and the two things act against one another.

Again, consider the series B_1 . Between 1 and 2 in this series the destruction of hydroxyl *lowers* the boiling-point, the destruction of molecular symmetry tends to raise it, the result being that the *difference* only of the two effects is small. Between 2 and 3 the destruction of hydroxyl and the restoration of symmetry act together, and the resultant effect is large.

The same effects may be noticed by comparing A_2 and B_2 in the same way, and also by comparing the first, second, and fourth members in the series A_3 and B_3 respectively.

XLV. *Notices respecting New Books.*

An Elementary Treatise on Modern Pure Geometry.

By R. LACHLAN. (London: Macmillan. 1893. Pp. x+288.)

MR. LACHLAN is a recognized master of the Geometrical craft, and the work before us well maintains his reputation. His primary object is to meet the new Cambridge Tripos regulations, in which provision is made for the introduction of a paper on "Pure Geometry." All that could fairly be looked for in such a paper is given by the writer, or is led up to by him. He has not, however, contented himself with such a limited supply as this would require, but he has written with a view to allure students on to the arcana of the science. After a careful perusal we have detected very few errata. On page 53, Ex. 4 is obviously a slip, and in line 3 from bottom for Bx read By , for Cx read Cz . Page 55 line 13 contains a small clerical error: the opening