

XXXII.—*On the Determination of High Boiling Points.*

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IN conducting a research on certain high boiling hydrocarbons we strongly felt the want of some method for determining with ease and with merely an approximate degree of accuracy the boiling points of those bodies which volatilise at temperatures too high to be measured by the mercurial thermometer. As it is probable that the same difficulty may have been experienced by others, it seemed to us that an account of the plan we adopted would not be uninteresting.

Our method consists in noticing whether certain salts melt on exposure to the vapour of the boiling substance. Now as the melting points of a large number of metallic salts have been determined by one of us (see preceding paper), we can in this way ascertain within certain limits the temperature of the boiling point in question.

For temperatures below 500° the substance may be boiled in an ordinary distillation flask, provided with a perforated cork, through which pass several capillary tubes containing salts which melt at known temperatures. If the substance boils above 500° , it is necessary to heat it in a tube of hard glass by means of the blowpipe. The tube is held in a slanting position, and passes through a hole in the centre of a piece of sheet iron, in order to protect that portion which is above the boiling liquid from the action of the flame. The capillary tubes containing the salts must also be made of hard glass. When the vapour of the boiling substance attacks glass, it is often difficult to observe whether the salts have melted. In this case it is advisable to protect the tubes from corrosion by inclosing them in thin glass sheaths.

In the following table the boiling points determined by our method (Column III) are compared with the actual temperature (Column IV) measured by a mercurial thermometer, the stem of which was completely immersed in the vapour of the boiling liquid. Column I contains the names of the substances, and II the salts used in determining the boiling point. The symbol + is used to indicate that the salt melts, and — to show that no change takes place.

I.	II.	III.	IV.	Remarks.
HgCl ₂	+ NaClO ₃ — NaNO ₃	302—316°	303°	{ In <i>Watts's Dictionary</i> the b.-p. given is 295°.
HgBr ₂	+ NaNO ₃ — KNO ₃	316—339	319	
SbCl ₃	+ AgNO ₃ — HgI ₂	218—241	221	{ According to Kopp, 223°. Capitaine, 230°.
Diphenyl.....	+ HgBr ₂ — Tl ₂ CO ₃	244—278	257	
Benzoic acid, m.-p. 121° ..	+ HgBr ₂ — Tl ₂ CO ₃	244—278	249	{ Kopp (<i>Jahresb.</i> , viii), m.-p. 121° 4; b.-p. 249° 2.

Now on referring to the list of melting points previously mentioned, it will be seen that but few of the salts melt below 300°, consequently we cannot bring the boiling point within such narrow limits as we can for higher temperatures. It must also be remembered that the method is only meant to be used for temperatures for which a mercurial thermometer cannot be employed, and in cases where merely an approximate knowledge of the temperature is required. The accuracy can obviously be increased by determining the melting points of a larger number of salts.

The following numbers show that good results are obtained at high temperatures:—

I.	II.	III.	Remarks.
Hg	+ NaNO ₃ + KNO ₃ — KClO ₃	339—359°	{ The boiling point of Hg has been carefully determined by Regnault (<i>Jahresb.</i> , xvi, 70) and by Dulong and Petit. The former found it to be 357° 25', and the latter 360°. Regnault (<i>Relation des Expériences</i> , &c., ii, 527) states the b.-p. of sulphur to be 447°. Hitortof gives the same number, but according to Dumas sulphur boils at 440°. Most of the determinations of the boiling points of S and Hg appear to have been made by means of the iodine pyrometer.
Sulphur purified by recrystallisation from carbon disulphide	+ TlI + ZnI ₂ — AgCl	446—451	

We have successfully applied our method in fractionating high boiling hydrocarbons, and in determining the boiling points of the following substances:—

I.	II.	III.	Remarks.
Anthracene, the specimen melts at 212.5°	+ KNO_3 - KClO_3	339—359°	Graebe and Liebermann (<i>Lieb. Ann.</i> , Supp. vii, 264) state that anthracene boils a little above 360° , but they do not describe how they measured the temperature.
HgI_2	+ NaNO_3 + KNO_3 - KClO_3	339—359	Prepared by triturating iodine and mercury in presence of a small quantity of alcohol.
AsI_3	+ ZnBr_2 - $\text{Ba}(\text{ClO}_3)_2$	394—414	Prepared by subliming a mixture of As and iodine.
BiCl_3	+ $\text{Ba}(\text{ClO}_3)_2$ + TiCl_4 - TiH	427—439	Two specimens, one prepared by dissolving bismuth in aqua regia, the other by burning the metal in chlorine gave the same results. The chloride decomposes slowly on long continued boiling; chlorine is evolved, and golden needle-shaped crystals are deposited.
BiBr_3	+ AgCl + $\text{Ti}_4\text{V}_2\text{O}_7$ + AgPO_3 - PbCl_2 - AgI	454—498	Prepared by the action of bromine on the pure metal.
SbI_3	+ PbI_2 + $\text{Ba}(\text{ClO}_3)_2$ - TiCl_4 - AgCl	414—427	Prepared by heating a mixture of iodine and antimony. The crude product was purified by sublimation over metallic antimony. The iodide melts at 171° (corr.), and decomposes slightly when boiled. The vapour has an intense dark red colour.
ZnBr_2	+ RbBr + Li_2CO_3 - KBr - NaBr	695—699	
PbCl_2	+ Na_2SO_4	Above 861	Prepared in the wet way; recrystallised from boiling water; attacks glass.
PbBr_2	—	—	Does not boil before the blowpipe. Attacks glass very rapidly.
CdCl_2	+ Na_2SO_4	Above 861	Two specimens gave the same results; a deposit separates out on boiling.

For the following substances a higher temperature is obtained by immersing the salts in the boiling liquid instead of in the vapour, whereas in the instances given above, the same result was got in both cases.

I.	In vapour.		In liquid.		Remarks.
	II.	III.	IV.	V.	
ZnCl ₂	$\left\{ \begin{array}{l} + \text{V}_2\text{O}_5 \\ + \text{CaBr}_2 \\ - \text{RbBr} \\ - \text{KBr} \end{array} \right\}$	$\left\{ \begin{array}{l} 676-683 \end{array} \right\}$	$\left\{ \begin{array}{l} + \text{KBr} \\ + \text{NaBr} \\ - \text{CaCl}_2 \end{array} \right\}$	$\left\{ \begin{array}{l} 708-719 \end{array} \right\}$	Attacks glass, and becomes turbid on boiling.
TiCl ₃	$\left\{ \begin{array}{l} + \text{Li}_2\text{CO}_3 \\ + \text{NaBr} \\ - \text{CaCl}_2 \\ - \text{KCl} \end{array} \right\}$	$\left\{ \begin{array}{l} 708-719 \end{array} \right\}$	$\left\{ \begin{array}{l} + \text{CaCl}_2 \\ - 2(\text{Pb}_2\text{V}_2\text{O}_7)\text{PbO} \\ - \text{KCl} \end{array} \right\}$	$\left\{ \begin{array}{l} 719-731 \end{array} \right\}$	Melts to a pale yellow liquid, which changes to a cherry red, and finally again turns yellow.
TlI ..	$\left\{ \begin{array}{l} + \text{NaCl} \\ + \text{Pb}(\text{PO}_3)_2 \\ - \text{Pb}_2\text{P}_2\text{O}_7 \\ - \text{Na}_2\text{CO}_3 \end{array} \right\}$	$\left\{ \begin{array}{l} 800-806 \end{array} \right\}$	$\left\{ \begin{array}{l} + \text{Pb}_2\text{P}_2\text{O}_7 \\ - \text{Na}_2\text{CO}_3 \end{array} \right\}$	$\left\{ \begin{array}{l} 806-814 \end{array} \right\}$	Decomposes slightly on boiling.
Cd ..	$\left\{ \begin{array}{l} + \text{KCl} \\ + \text{MoO}_3 \\ - \text{NaCl} \\ - \text{Na}_2\text{CO}_3 \end{array} \right\}$	$\left\{ \begin{array}{l} 763-772 \end{array} \right\}$	$\left\{ \begin{array}{l} + \text{MoO}_3 \\ \text{NaCl begins to melt.} \end{array} \right\}$	$\left\{ \begin{array}{l} 772 \end{array} \right\}$	Dewille and Troost (<i>Compt. rend.</i> , xlix, 240) give 860° as the boiling point of Cd, but how this number was obtained is not clearly stated.

We hope shortly to determine the boiling points of potassium, sodium, magnesium, thallium, and other metals, with special reference to their bearing on Mendelejeff's law of the periodicity of the elements.
