LX.—*The Vapour Pressures of Mercury.*

By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University
College, Bristol.

IN the determinations of the vapour pressures of mercury (Ramsay and Young, *Trans.*, 1886, **49**, 37), the highest temperature was obtained by heating the metal with the vapour of boiling sulphur, and in calculating the results the boiling point of sulphur given by Regnault (*Mémoires*, vol. **26**) was taken as correct. Callendar and Griffiths have, however, recently redetermined the boiling point of sulphur with an air thermometer, and have found it to boil at a temperature nearly 4° lower than Regnault did. Their experiments have evidently been

carried out with great care, and they point out that Regnault himself did not place very great confidence in the values he obtained.

Again, the boiling point of mercury determined by Callendar and Griffiths by their platinum thermometer, calibrated by means of an air thermometer, is nearly 2° lower than that given in the paper referred to.

I have employed the vapour of mercury as a jacket in the determination of the critical temperatures and pressures of chlorobenzene and of stannic chloride (not yet published) and in both cases the temperature appeared to be rather too high. In the case of stannic chloride, constants could not be calculated for Biot's formula which would reproduce both the pressures at 240 — 280° (determined by means of bromonaphthalene) and those at 310 and 320° , in the determination of which mercury was employed. It has been pointed out in various papers by Ramsay and myself that errors in the determination of the vapour pressures of a substance may be discovered by comparing the absolute temperatures with those of a second substance at the same series of pressures. The ratios of the absolute temperatures mapped against the temperatures of one of the two substances should give a straight line, at any rate for a moderate range of pressure, and if there is pronounced curvature it may be concluded that the vapour pressures of one or other substance require correction. The existence of considerable errors in Regnault's vapour pressures of mercury and in Landolt's vapour pressures of the fatty acids was discovered in this way.

On the other hand, it may, of course happen that a straight line is obtained even when the determinations are faulty, for the errors may be of such a nature as to give a straight line somewhat different in direction from the true one. This appears to be the case with sulphur, for the ratios of the absolute temperatures, as determined by Regnault, to those of carbon bisulphide under equal pressures, do give a straight line when mapped against the temperatures of carbon bisulphide.

The ratios of the absolute temperatures of dibenzyl ketone to those of both water and benzene give very decided curves if the vapour pressures of mercury given in the paper referred to be taken as correct.

All these facts point to the conclusion that the vapour pressures of mercury based on Regnault's boiling point of sulphur are too low at high temperatures, in other words, that the boiling points are too high.

The calculations of the vapour pressures of mercury, made by Ramsay and myself, were based on the following experimental data:—

1. Direct determination of vapour pressures of mercury in a U-tube closed at one end and connected at the other with a gauge and barometer. The tube, containing mercury, was heated with bromonaphthalene under atmospheric and reduced pressure, and with methyl salicylate under atmospheric pressure.

2. Regnault's determinations of the boiling point of mercury under atmospheric pressure.

3. Direct determinations of vapour pressure at the boiling point of sulphur in a special apparatus.

1. In the case of methyl salicylate there may be a small error, for this substance has not been found to give such good results as the other pure liquids (Ramsay and Young, *Trans.*, 1885, **47**, 640) and I have recommended the employment of quinoline in place of it (*Trans.*, 1889, **55**, 483).

The pressures at 270° and 280° with bromonaphthalene are in all probability very nearly correct, for this substance has been repeatedly used for heating purposes, and the results obtained do not point to the existence of any error, or at most an extremely small one at these temperatures.

2. Regnault's boiling points of mercury are far from satisfactory, the difference between the highest and lowest results amounting to nearly 2°.

3. The determinations of the boiling point of sulphur, and also of mercury, by Callendar and Griffiths may probably be taken as the best yet obtained, and I have, therefore, made use of them in the new calculations.

On account of the possibility of error with methyl salicylate I have determined the vapour pressures of mercury with quinoline and with aniline, boiling under atmospheric pressure, by the same method as that previously employed. The results, each of which is the mean of a considerable number of readings, are given in the table below.

	Temperature.	Pressure.	Calculated from tables by Ramsay and Young.
Aniline.....	183·8	9·94 ± 0·083	9·80
Same with larger apparatus	183·7	9·85 ± 0·046	
Quinoline.....	236·9	51·85 ± 0·06	52·30

These results show that at low temperatures the results given in the tables require very little alteration.

Ratios of the absolute temperatures of mercury to those of water at equal pressures were then calculated and mapped against the temperatures of water. The points so obtained fall very nearly on a

straight line, and the absolute temperatures of mercury are reproduced very well by the following formula:—

$$R = 1.6004 + 0.000882t,$$

where R is the ratio of the absolute temperature of mercury to that of water at any pressure, and t is the temperature of water on the centigrade scale at the same pressure.

A comparison is given below of the temperatures of mercury given by this formula with the data obtained experimentally, including the boiling point of mercury determined by Callendar and Griffiths, and the results by Dr. Ramsay and myself with sulphur, recalculated on the basis of Callendar and Griffiths' boiling point of that substance.

Press.	Absolute temp. of water.	Ratio calculated from formula.	Calculated temp. of mercury.		Observed temp. of mercury.	Differences.	
			Absolute.	Cent.		Temp.	Press.
9.87	284.1	1.6102	457.45	184.45	183.75	-0.7	+0.23
34.4	304.5	1.6282	495.8	222.8	222.15	-0.65	+0.65
51.85	311.95	1.6348	509.95	236.95	236.95	0.0	0.0
124.35	329.2	1.6500	543.2	270.2	270.3	+0.1	-0.3
157.15	334.2	1.6544	552.9	279.9	280.2	+0.3	-1.1
760.0	373.0	1.6886	629.85	356.85	356.76	-0.09	+1.2
2896.9	415.25	1.7259	716.7	443.7	443.15	-0.55	+20.7
2904.5	415.35	1.7260	716.9	443.9	444.15	+0.25	-9.4

For temperatures between 236° and 444° , the results given by the above formula are very good; but at lower temperatures the vapour pressures given in the paper by Dr. Ramsay and myself agree rather better with the observed values.

The formula $R = 1.6004 + 0.000882t$ has been employed in calculating the temperatures of dibenzyl ketone, given in the tables in the paper on the vapour pressures of that substance under the heading "Corrected." The ratios of the corrected absolute temperatures of dibenzyl ketone to those of water at the same pressures give an approximately straight line, very much better than that obtained with the uncorrected values.

The temperatures of dibenzyl ketone given by the formula

$$R = 1.5842 + 0.0003283t$$

(where t is the temperature of water in centigrade degrees), are compared in the following table with those calculated by means of Biot's formula at the same pressures:—

Pressure.	Temperature.		Difference.
	Biot	From ratios.	
70	235·05	234·8	-0·25
100	246·9	246·9	0·0
150	261·25	261·25	0·0
200	272·05	272·45	+0·4
300	288·2	288·4	+0·2
500	310·45	310·55	+0·1
760	330·55	330·15	-0·4

The vapour pressures of mercury were recalculated for each 10° from 180° to 480°, and for each degree from 330° to 360° by means of the formula

$$R = 1·6004 + 0·000882t,$$

which may be converted into

$$t = \sqrt{1133·8T' + 594055} - 1043·75,$$

where t is the centigrade temperature of water corresponding to an absolute temperature, T' , of mercury at the same pressure. The temperature of water, t , being calculated, it is only necessary to refer to a table of the vapour pressures of water to find the required pressure.

The results are given in the following tables :—

Table of Vapour Pressures of Mercury.—I.

T.	P.	T.	P.	T.	P.	T.	P.
180	8·41	260	96·46	340	559·1	420	2085·0
190	11·98	270	124·0	350	672·5	430	2402·5
200	16·81	280	157·8	360	803·7	440	2757·0
210	23·22	290	198·9	370	954·7	450	3150·5
220	31·64	300	248·6	380	1127·5	460	3586·0
230	42·56	310	308·0	390	1325·0	470	4067·0
240	56·55	320	378·5	400	1548·5	480	4596·0
250	74·26	330	461·7	410	1801·0	—	—

II.

T.	P.	T.	P.	T.	P.	T.	P.
330	461·7	338	538·4	346	625·1	354	722·7
331	470·8	339	548·6	347	636·7	355	735·7
332	480·0	340	559·1	348	648·4	356	749·0
333	489·3	341	569·7	349	660·4	357	762·3
334	498·8	342	580·4	350	672·5	358	775·9
335	508·5	343	591·3	351	684·8	359	789·7
336	518·3	344	602·4	352	697·3	360	803·7
337	528·3	345	613·7	353	709·9	—	—

NOTE BY WILLIAM RAMSAY, Ph.D., F.R.S.

Professor Young has kindly sent me this note for revision and criticism, on the ground that the former determinations were made by both of us, and that an alteration in the results should have the assent of both authors. I am convinced that, owing to the more accurate determination of the boiling point of sulphur at normal pressure made by Messrs. Callendar and Griffiths, the alterations in the numbers for the vapour pressures of mercury suggested in the foregoing paper are necessary. This affords another instance of the danger of accepting Regnault's data without criticism. In spite of the very great care he expended, the results of his investigations are by no means perfect, and further revision will doubtless lead to the discovery of other inaccuracies.