LIX.—*On the Vapour Pressures of Dibenzyl Ketone.*

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In order to obtain constant temperatures above 280°, the vapour of mercury boiling under known pressures may be employed, but there are serious objections to this substance, and it seems doubtful whether absolutely accurate results can always be obtained with it. Up to 306° benzophenone may be employed, and this substance is strongly recommended by Crafts (*Amer. J. Sci.*, **5**), but the range of temperature above 280° is small.

It seemed probable that dibenzyl ketone might give good results, and I have therefore prepared some of this substance by a method described in the preceding paper.

The boiling point of dibenzyl ketone is 330·55° under normal pressure; there is thus a convenient range of temperature—just 50°—between the boiling points of this substance and of bromonaphthalene.

The ketone is a stable substance, for after several hours heating at temperatures between 260° and 330°, no alteration in the boiling point was observed. It is true that a little decomposition had taken place, for the ketone was no longer colourless, and on subsequent distillation the temperature, though very nearly constant for some time, did not remain so throughout. The rise of temperature was 0·3° after about three-fourths of the substance had distilled over; afterwards the rise was more rapid, and a little tarry liquid was left in the bulb. The product of decomposition possesses, however, a higher boiling point than the ketone, and was not present in sufficient quantity to affect the temperature of the vapour above the liquid

while the measurements were being made. The first and second series of determinations were made with different samples of the ketone, which were afterwards mixed together, and a portion of this was employed for the third and fourth series. The last series of determinations was therefore made with a portion of the ketone which had been boiled under various pressures for several hours, but the results agreed perfectly with those previously obtained.

The low melting point, 33·9°, of the ketone is also convenient, whilst, on the other hand, the readiness with which it crystallises from ether greatly facilitates its purification. Dibenzyl ketone may therefore be recommended for obtaining constant temperatures between 280° and 330°.

In the determinations of the vapour pressures of the substance, temperatures from 230° to 280° were read on an ordinary thermometer, standardised by means of bromonaphthalene. For higher temperatures a mercury vapour pressure thermometer was employed.

In the first two series of determinations the liquid was boiled in a slightly modified distillation bulb, the neck of which was sufficiently long to allow of the whole of the mercury in the thermometer being heated by the vapour. The lower part of the neck of the distillation bulb was covered with asbestos, to reduce the loss of heat by radiation.

The apparatus employed for the higher temperatures was similar to that described by Dr. Ramsay and myself (Trans., 1885, **47**, 651). The tube in which the ketone was boiled was 510 mm. long, and 41 mm. in internal diameter. At each temperature from two to six readings were, as a rule, taken, and the mean results are given in the tables.

In calculating the temperatures, the vapour pressures of mercury determined by Ramsay and myself (Trans., 1885, **49**, 37) were first employed, but it seems probable that, owing to an error in Regnault's determination of the boiling point of sulphur, the vapour pressures of mercury, which at high temperatures depend on those of sulphur, require some alteration. The point is discussed in a paper on the Vapour Pressures of Mercury.

The temperatures under the heading "corrected" have been finally adopted.

The pressures are in millimetres of mercury at 0°, and the temperatures are those of an air thermometer.

Experimental Results.

Temperatures with Ordinary Thermometer.

Series I.—Sample of ketone obtained by heating calcium phenylacetate in a combustion tube.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
230·55	60·3	249·1	105·6	270·35	191·7
232·85	64·95	253·1	118·7	274·45	213·5
236·05	71·5	257·85	136·1	278·0	234·2
240·2	81·15	262·55	155·0	—	—
244·3	91·8	266·6	173·25	—	—

Series II.—Sample of the ketone obtained by new method.

237·55	75·45	254·95	125·35	270·65	193·45
242·0	85·8	258·65	139·2	274·4	213·7
246·35	97·55	262·8	156·5	277·45	231·2
250·6	111·15	266·7	174·05	—	—

Temperatures with Mercury Vapour-pressure Thermometer. Series I.

Temp.	Corrected.	Pressure.	Temp.	Corrected.	Pressure.
260·65	260·8	147·9	293·55	293·4	338·3
265·8	265·8	169·75	303·3	303·0	422·3
270·25	270·3	192·25	317·4	316·85	570·8
276·95	276·85	227·5	330·8	330·1	746·45
284·65	284·55	276·0	—	—	—

Series II.

261·0	261·1	150·6	299·95	299·7	392·1
268·9	268·7	183·35	308·35	307·95	471·5
274·35	274·25	213·4	314·55	314·1	537·2
282·8	282·75	262·7	322·15	321·55	630·1
288·9	288·7	304·6	330·85	330·1	747·8

The agreement between the four series of results is very satisfactory.

The logarithms of the pressures were mapped against temperatures, and the logarithms of pressures corresponding to even temperatures read off. Constants for Biot's formula ($\log p = a + b\alpha^t$) were then calculated, and from these the pressures corresponding to definite temperatures—each 10° from 230° to 330°, and each degree from 280° to 332°—were calculated.

The constants for Biot's formula are—

$$a = 4{\cdot}75779,$$
$$b = -2{\cdot}981088 \quad \log b = 0{\cdot}4743748,$$
$$\log \alpha = \bar{1}{\cdot}9980014,$$
$$t = t^\circ \text{ C.} - 230.$$

The calculated pressures are given in the following tables:—

I.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
230	59·80	260	144·90	290	313·3	320	613·2
240	81·45	270	189·65	300	396·0	330	752·0
250	109·35	280	245·20	310	495·2	—	—

II.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
280	245·2	294	344·5	308	474·0	322	639·3
281	251·4	295	352·7	309	484·5	323	652·6
282	257·7	296	361·1	310	495·2	324	666·2
283	264·2	297	369·6	311	506·2	325	679·9
284	270·8	298	378·2	312	517·3	[illegible]	693·9
285	277·5	299	387·0	313	528·6	327	708·1
286	284·4	300	396·0	314	540·1	328	722·5
287	291·4	301	405·1	315	551·8	329	737·2
288	298·5	302	414·4	316	563·6	[illegible]	752·0
289	305·8	303	423·9	317	575·7	331	767·2
290	313·3	304	433·6	318	588·0	332	782·5
291	320·9	305	443·4	319	600·5	—	—
292	328·6	306	453·4	320	613·2	—	—
293	336·5	307	463·7	321	626·2	—	—