CIX.—*The Apparent Influence of an Electric Field on the Boiling Point of Benzene.*

By JOHN WILLIAM SMITH.

IT has been shown by Baker (J., 1928, 1051) that if benzene is introduced into tubes containing two parallel platinum plates, which are connected to a 400-volt battery for some hours, the boiling point of the benzene is raised from 80° to 91°; and similar changes are observed in surface tension. These changes were attributed to changes in the internal complexity of the benzene owing to the moisture being unable to form into droplets, which were supposed, on Sir J. J. Thomson's theory (*Phil. Mag.*, 1893, **36**, 320), to cause the so-called normal behaviour of the liquid. Subsequently, Smits (J., 1928, 2399) found that, although the apparent boiling point was raised considerably when the tube was heated in an oil bath, the liquid still boiled at the normal temperature when the tube was heated directly with a small flame, and that the vapour pressure was unchanged; hence he concluded that Baker's high boiling points were due to superheating, which is induced by the removal of electrically charged dust particles by the electric field, and is facilitated when heating is carried out in a bath. The removal of dust particles was also supposed to account for the abnormalities in surface tension.

Although the experiments now described confirm those of Smits, several other observations have been made which are considered worthy of record.

EXPERIMENTAL.

The benzene used was Kahlbaum's "thiophene-frei," and contained no detectable amount of thiophen. After being frozen out twice, it was distilled, and the middle fraction was stored over phosphoric oxide for a few days and distilled from this reagent before use.

Baker's simple experiment was first repeated, the benzene being sealed into a tube containing two parallel electrodes of platinum foil and two thermometers, one suspended in the liquid and the other in the vapour. The top of the tube was drawn out to a long capillary of about 2 mm. diameter, which was bent twice at right angles. After the tube was charged with the benzene, the end of this capillary tube was sealed, and a *P.D.* of 540 volts applied to the electrodes. After a week the capillary tube was opened under dry mercury, and the bulb immersed in an oil bath, the temperature of which was raised gradually. At about 80°, considerable evaporation occurred from the benzene, as shown by refluxing down the walls of the vessel, but no visible ebullition occurred. At 84·5°, bubbles began to rise from the electrodes, but the thermometer in the vapour registered 80°. One of the leads then accidentally became dislodged, whereupon boiling instantly ceased, but resumed as soon as the lead was restored. Hence the leads were removed and the heating continued. The temperature rose to 85·5° before ebullition recommenced. The temperature of the liquid fluctuated between 85° and 86°, but the thermometer in the vapour remained at 80°. If the leads were restored whilst gentle ebullition was occurring at 85·5°, the liquid boiled much more violently, the temperature falling to 84·5°, but became quiescent again as soon as they were removed.

Another specimen in a similar tube boiled at 87°, and continued at that temperature while most of the benzene was boiled away. When only a little was left, however, the temperature rose to 93°. The highest temperature recorded in the vapour was 81°, but, as this was reached when only very little liquid remained, it was probably due to some superheating of the vapour.

An experiment was carried out in the same tube under similar conditions with benzene which had not been subjected to the electric field. The boiling point as registered by the thermometer in the liquid was 80·5°, and that in the vapour 80°. When only a very small amount of liquid remained, the temperature in the liquid rose to 81°, but the vapour temperature was still 80°. In this case, however, the temperature of the bath was only slightly higher than that of the liquid in the tube, whereas in the case of the benzene which had been under the electric field the bath had to be taken to a much higher temperature (105°) in order to cause ebullition. It has been observed throughout these experiments that after a temperature of about 80° was passed, the temperature of the liquid in the bulb remained always considerably below that of the bath, although comparatively thin-walled glass tubes were employed. This is attributed to the rapid evaporation from the surface of the liquid, and the return of condensed liquid into the bulb. In many cases this effect made it difficult to raise the temperature of the benzene sufficiently to cause it to boil visibly.

A series of experiments was also carried out in order to test whether any change in vapour pressure occurred on subjecting the liquid to an electric field. Both mercury and glass-spring indicator gauges were employed, but the results were entirely negative, although electric fields up to about 1500 volts per cm. were applied and the temperature of measurement was varied from 0° to 80°. Boiling-point observations showed that the presence of mercury was detrimental to the production of the phenomenon, and also that less effect was observed when there was a considerable " dead space " not under the electric field at the side of and behind the electrodes.

In one apparatus in which a glass-spring indicator was employed, a *P.D.* of 440 volts was applied to electrodes 1 cm. apart in the benzene for a month without causing any change in vapour pressure. A side bulb was then immersed in ice, and after about one-third of the liquid had condensed in it, the bulb was sealed off, a fraction of the liquid being thus removed. The rate of attainment of the previous vapour pressure, however, was almost exactly the same as when a fraction was removed under similar conditions before application of the field. This behaviour contrasts strongly with that of intensively dried liquids, in which the rate of attainment of a constant vapour pressure is extremely slow.

In order to avoid the presence of any " dead space," another type of cell was employed. A flat bulb was constructed with parallel sides, about 7 mm. apart, platinum wires being sealed through each face. In order to form two parallel silver plates on these walls, paraffin wax was run round the edge of the bulb, so as to form a thin but continuous layer. The interior of the bulb was then silvered. The paraffin wax was removed by repeated washing with benzene. Thus the silver deposits on the two faces remained effectively insulated from one another. Again, with this type of vessel, no vapour-pressure change could be detected after connecting the electrodes to a *P.D.* of 400 volts for a month. Boiling-point determinations with such a cell furnished some interesting results, however, which serve to throw some light on the cause of the high apparent boiling point.

A small thermometer was suspended in the liquid by means of a platinum wire, so that its bulb was equidistant from the faces and approximately in the centre of the liquid. Without the top of the tube being sealed, a *P.D.* of only 220 volts was applied to the electrodes, but after two or three days the apparent boiling point was raised considerably. The heating was carried out by means of an oil bath, and on some occasions the temperature of the liquid in the bulb could be raised to 104° before ebullition commenced. This occurred suddenly, and the temperature fell a few degrees, after which the liquid boiled steadily at 96°. As has been found in all these experiments, the bubbles arose from one point on one of the electrodes, in this case from one of the platinum wires sealed through the wall of the vessel. If, however, whilst the temperature was about 90°, the liquid was stirred vigorously with the thermometer, bubbles escaped violently from the liquid in the tube, and the temperature fell. As soon as agitation was discontinued, however, the ebullition ceased, and the temperature began to rise again.

The more vigorously the liquid was stirred, the lower the temperature became. In this way it was possible to lower the temperature of the liquid from 94° to 82°. The actual temperature at which the unagitated liquid boiled was by no means reproducible. After the electric field had been applied for a day, the boiling point did not appear to rise progressively with time, but, in general, the unagitated liquid attained steady boiling at some temperature between 90° and 100°, and this ebullition showed none of the characteristics of superheating as generally observed. When the liquid to which the field had not been applied was kept boiling gently at 80·5°, no rise in this boiling point could be observed when the field was applied for four hours. Thus it would appear that the agitation caused by the boiling destroyed the effect which the electric field tends to produce.

The boiling point found when the bulb was heated directly with a small flame was in complete accordance with the observations of Smits (*loc. cit.*), for it was always unaltered whatever the duration of the electric field, and even with specimens of benzene which boiled steadily at temperatures as high as 96° when heated in an oil bath.

Hence it appears certain that Baker's observation of a rise in boiling point after application of an electric field was due, as suggested by Smits, to superheating induced by the removal of charged nuclei from the system.

Summary.

When an electric field is applied to benzene in a tube heated by means of an oil bath, the apparent boiling point, as registered by a thermometer in the liquid, rises, as has been shown by Baker. The vapour temperature, however, retains its normal value. This effect is not observed when the tube is heated directly with a small flame. The effect is considerably reduced by stirring, and the more so the more vigorous the agitation. No change in vapour pressure occurs when benzene is subjected to an electric field. The effect observed by Baker is attributed to superheating.

In conclusion, the author desires to express his great indebtedness to the Department of Scientific and Industrial Research for grants during the tenures of which this work was carried out; also to Professor F. G. Donnan, F.R.S., at whose suggestion this work was commenced, for his kindly advice and criticism.

THE SIR WILLIAM RAMSAY LABORATORIES OF
INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, March 6th*, 1929.]