

*Liquid Metals. Part II.\* The Surface Tension of Liquid Sodium : the Drop-volume Technique.*

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The surface tension of liquid sodium in an atmosphere of pure argon has been measured over the temperature range 110–220° by a drop-volume method, which is described. The temperature coefficient of tension is  $-0.1$  dyne  $\text{cm}^{-1}$  degree $^{-1}$ , and extrapolation of results to the melting point of sodium gives  $\gamma = 202$  dynes  $\text{cm}^{-1}$ . Results are compared with those obtained by the vertical-plate method.

PART I \* described the measurement of the surface tension of liquid sodium by the vertical-plate technique, with plates of zinc and copper and an atmosphere of pure argon. This method gave  $\gamma = 195$  dynes  $\text{cm}^{-1}$  at the melting point of sodium (98°), with a temperature coefficient of  $-0.1$  dyne  $\text{cm}^{-1}$  degree $^{-1}$ . The method involves the exposure of the sodium surface to the argon atmosphere for periods of several minutes, but the value obtained agrees closely with the value 191 dynes  $\text{cm}^{-1}$  at 98° obtained by Taylor (A.E.R.E. Report M/R.1247, 1953; *J. Inst. Met.*, 1954–55, **83**, 143) using the maximum bubble-pressure method, so that there appear to be no errors resulting from contamination of the sodium surface. However, in view of the importance of this value in the study of the wetting of solids by liquid sodium, it was desirable to confirm the value of the tension by using a different method. In the first determination of the surface tension (Quincke, *Ann. Physik*, 1868, **135**, 621) the drop-weight technique was used, but the method has not been employed since then; it was therefore also of interest to ascertain to what extent the high value obtained by Quincke (252 dynes  $\text{cm}^{-1}$  at the melting point) was due to the use of carbon dioxide as an "inert" atmosphere.

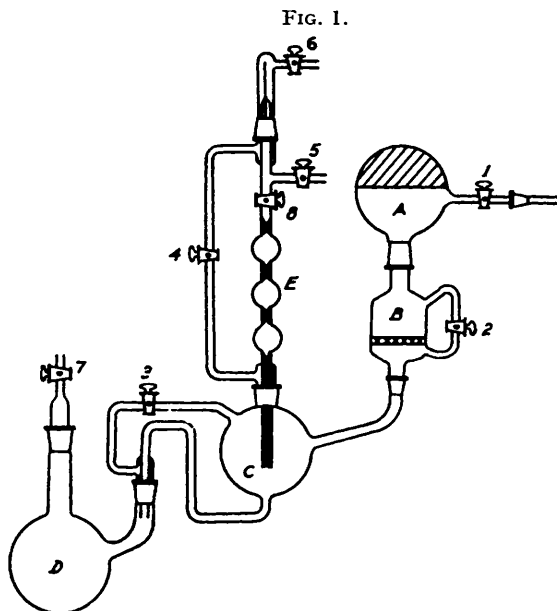
#### EXPERIMENTAL

Purification of sodium and argon was carried out as described in Part I (*loc. cit.*). Values used for the density of sodium were also given therein. A diagram of the drop-volume apparatus used is shown in Fig. 1. It was constructed in Pyrex glass, the ground-glass joints being held in place by metal clips (not shown) to enable the apparatus to withstand an internal pressure of argon. Taps were lubricated with molybdenum disulphide (Ragosine Anti-scuffing powder). Silicone grease cannot be used in any part of the apparatus, since even traces of it have a considerable effect on the surface properties of liquid sodium: drops of the metal form irregularly on the orifice, and the apparent tension is reduced to as little as half of the true value. The apparatus consists essentially of a drop-volume pipette, with devices for filling the pipette with sodium through the orifice and for removing excess of sodium. The pipette *E* has three bulbs of known volume (each about 2 ml.). The orifice (internal radius 0.118 cm.) was prepared by making a small scratch on a capillary tube, and then breaking the tube to give a sharp edge; drop formation was more satisfactory from this type of orifice than from a ground orifice. Since clean sodium does not wet glass, the drops formed on the inside rim of the orifice, and the physical constants of the pipette were checked by determination of the interfacial tension of chlorobenzene and carbon tetrachloride against water, where the same conditions apply. When used for high-temperature measurements with sodium, the bulb volumes and orifice radius were corrected for thermal expansion of the glass. Surface tensions were calculated by the usual formula  $\gamma = mgF/r$ , the correction factor *F* being determined from the tables of Harkins and

\* Part I, *J.*, 1954, 2861.

Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499). The orifice size used is near the lower practicable limit. Owing to the high surface tension of liquid sodium, there is a sharp change in internal pressure as a drop falls away; with small orifice diameters the drops were rapidly ejected from the orifice, the metal recoiled far into the orifice tube, and it was not possible to control drop formation adequately. The top of the pipette was drawn off to a fine thread, so that during an experiment the sodium flowed slowly from the bulbs under gravity.

*Method.*—The component parts of the apparatus were cleaned, dried at 200–250°, and assembled as in Fig. 1. The whole assembly was then placed inside a thermostatically controlled air-oven, with the argon lead to tap 1 passing through the side of the oven. The apparatus was then flushed with pure argon for 2 hr. at 0.5 l./min. To allow argon circulation, taps 1, 2, 3, 4, and 8 were kept open, and the gas was allowed to escape from taps 5, 6, and 7 in turn. This argon flow was continued throughout the experiment. With taps 2, 5, and 6 closed, the oven was raised to a temperature about 10–20° below that selected for the measurements. The sodium (previously purified) contained in flask *A* melted and flowed on to the glass sinter plate (grade 3, diam. 7 cm.) in the filter vessel *B*. When the plate was covered, argon pressure forced



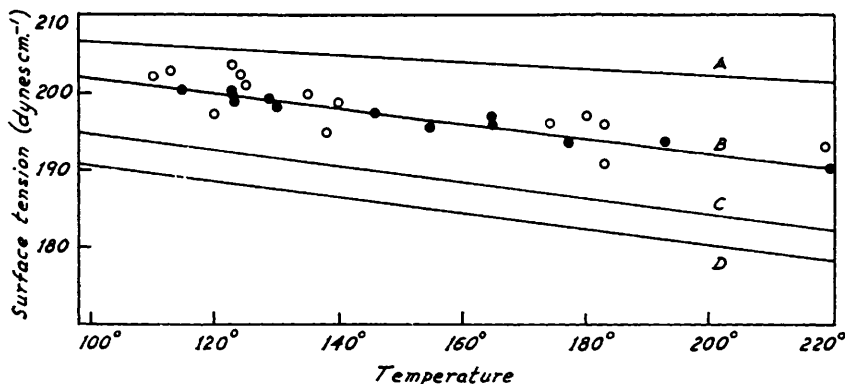
the sodium through the plate and into vessel *C*. This was continued until the sodium in *C* rose about 2 cm. above the orifice level; the flow of sodium was stopped by opening tap 2. The temperature of the oven was then raised to that at which the measurements were to be made. On closing taps 4 and 7, argon pressure increased in *C*, forcing sodium through the orifice into the bulbs of the pipette. When these were filled, tap 8 was closed and taps 4 and 7 were opened to release argon pressure. The sodium remaining in vessel *C* was removed by closing tap 3, a syphon being created between vessels *C* and *D*. The sodium flowed into *D*, leaving a clean orifice. When tap 8 was opened the sodium in the pipette flowed slowly under gravity, from the orifice, and the number of drops (about 20) obtained from each bulb was counted. By measuring the time of formation of each drop it was possible to calculate, with sufficient accuracy, the drop fractions formed as the sodium level passed the bulb calibration marks. Variation in times of drop formation produced no significant difference in the measured tension provided the time exceeded about 12 seconds. This is illustrated by the following data:

Time of drop formation (sec.) .....	32	47	140	180	240
$\gamma$ (dynes cm. <sup>-1</sup> ) .....	198.5	198	199	199	198.5
Temperature .....	129°	130°	123°	123°	123°

Most of the results recorded in Fig. 2 were obtained at flow rates of about 60 sec. per drop. It was sometimes found possible to filter more sodium into *C*, to refill the pipette, and to repeat a measurement before dismantling the apparatus.

*Dismantling Procedure.*—The greatest risk of fire arises during the dismantling of the apparatus. Any sodium remaining in filtration unit *B* was transferred through the filter plate into vessel *C* by closing tap 2 for a short time. The sodium in *C* was then transferred into vessel *D* by closing tap 3. The apparatus was removed from the oven, the exit tube of vessel *D* removed, and the sodium poured into a steel mould by tilting the whole assembly; the argon flow was turned off, and vessel *D* quickly stoppered to prevent ingress of oxygen. When cool, the apparatus was dismantled, and the sodium removed by immersing the component parts in ethyl alcohol. Filtration unit *B* was cleaned with glacial acetic acid, since the sintered plate rapidly disintegrated in the presence of hot alcoholic sodium ethoxide solution.

FIG. 2.



- A*, Poindexter and Kernaghan, *Phys. Rev.*, 1929, **33**, 837 : sessile drop.  
*B*, Present results : drop volume.  
*C*, Addison, Kerridge, and Lewis, Part I, *loc. cit.* : vertical plate.  
*D*, Taylor, *loc. cit.* : maximum bubble pressure.

### RESULTS

Surface-tension values over the temperature range 110—220° are given in Fig. 2. The experimental routine is a complicated one and, when adjustments were made during an experiment which might possibly influence the accuracy of the results, the latter are shown in Fig. 2 as open circles; results from experiments regarded as ideal are shown as black points. Extrapolation to the m. p. of sodium gives a value of 202 dynes cm.<sup>-1</sup>. The temperature coefficient is  $-0.1$  dynes cm.<sup>-1</sup> degree<sup>-1</sup>, in agreement with the vertical plate results (line *C*) but the tension values are 7 dynes cm.<sup>-1</sup> higher. Part of this small difference may be attributable to the various correction factors necessary in each method, but the general agreement in the results shows that the drop-volume method, using a glass orifice, is acceptable for the determination of the surface tension of liquid sodium. If it is assumed that traces of sodium oxide on the metal surface are able to lower the surface tension, then it is to be expected that values determined by the drop-volume method, in which a fresh surface is continually formed, would be somewhat higher than with the vertical-plate method, in which the surface is exposed for longer periods. This aspect will be discussed in greater detail in a later paper on the influence of oxide films on the surface tension of liquid sodium.

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