Liquid Metals. Part III. The Influence of Oxide Films on the Surface Tension of Liquid Sodium.*

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The drop-volume technique has been used to determine the changes in surface tension of liquid sodium which occur when dry air is introduced into the argon atmosphere surrounding the metal drops. At 180°, the surface tension decreases linearly with partial pressure of oxygen, from 194 to 186 dynes/cm. A minimum occurs at an oxygen partial pressure of 2×10^{-4} atm., after which the tension can increase to very high values. The tension minimum is related to the change from a soluble to an insoluble film of sodium oxide at the metal surface.

THE formation of oxide films at the metal surface represents the main source of error in surface-tension determinations on liquid metals, yet very little is known of the extent to which such films influence the tension. Taylor (A.E.R.E. Report M/R 1247; *J. Inst. Met.*, 1954—55, **83**, 143), using the maximum bubble pressure method and an argon atmosphere, observed that the surface tension of liquid sodium increased on addition of oxygen to the argon (by 21 dynes/cm. in the presence of 5% of oxygen); it was suggested that the high values of tension obtained by Poindexter and Kernaghan (*Phys. Rev.*, 1926, **23**, 820; see also Part II, *J.*, 1955, 2262) resulted from the presence of an oxide film, but there is no direct proof of this. According to Portevin and Bastien (*Compt. rend.*, 1936, **202**, 1072) the surface tension of pure liquid aluminium can be increased by a factor of two by oxidation of the surface. In contrast, Davis, Mack, and Bartell (*J. Phys. Chem.*, 1941, **45**, 846) observed that the surface tension of liquid gallium is reduced from 735 to 300 dynes/cm. at 30·5° on admission of air to the system, and an oxide film could be responsible for this change. Measurements on solid silver at a temperature just below its melting point also suggest a lowering of surface tension by oxide films (Buttner, Funk, and Udin, *ibid.*, 1952, **56**, 657).

Since the surface tension of fused metal oxides is normally much lower than that of the corresponding metals (see Bondi, *Chem. Rev.*, 1953, **52**, 417) the presence of oxide at the surface would be expected to lower the surface tension of the metal. Published data show no general agreement on this issue; this is considered to result from the dual role which oxide films can play. If the oxide is present in such small quantity that it will dissolve in the liquid metal, a soluble film will be formed which will lower surface tension to an extent which will depend on, *inter alia*, the solubility of the oxide. Continued formation of oxide beyond the solubility limit will give rise to an insoluble film; if the oxide concerned is cohesive in nature, it can act to some extent as a separate phase, and the apparent tension then represents the sum of the tension of the liquid metal and the tension in the separate cohesive film. As the quantity of oxide present is increased, the surface tension of a liquid metal may therefore pass through a minimum.

The purpose of the work described in this paper was to test this hypothesis in the case of liquid sodium. The solubility of sodium monoxide in the metal is very small [0·004 wt. % of Na_2O at 200°, Liquid Metals Handbook, NAVEXOS P-733 (Rev.), 2nd Edn., 1952, p. 114] but the cohesion of the oxides is high.

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* Part II, *J.*, 1955, 2262.

EXPERIMENTAL

The drop-volume technique described in Part II was used. The pure argon atmosphere was contaminated with known amounts of dry air, and the resulting change in surface tension determined from the change in drop volume of sodium.

Contamination of the argon was carried out as follows. Argon–air mixtures of known composition (2—30% of air by volume) were prepared in a 5-l. aspirator, and kept under slight pressure by connecting the aspirator with a second elevated vessel containing water. The rate of flow of gas mixture was controlled by an Ermeto fine-control valve; the gas passed successively through a phosphoric oxide drying tube, a sintered glass plate which acted as dust filter, and a flow meter. It then entered the main argon stream at a position as near as possible to that at which the argon entered the drop-volume apparatus, so that its presence was rapidly reflected in change of behaviour of the metal drops. The main argon stream flowed at a rate near 1300 ml./min. throughout the experiment; the argon–air mixture flow rate was in the range 10—70 ml./min. (measured with an accuracy of 1 ml./min.) and from these quantities the oxygen partial pressures quoted in Figs. 2 and 3 were calculated.

FIG. 1.

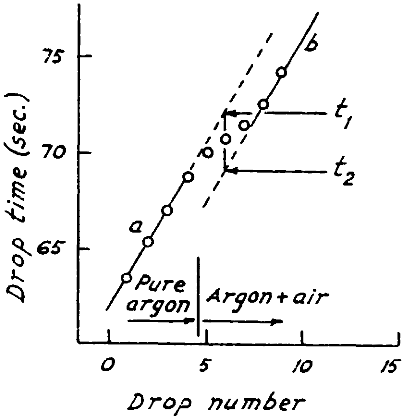


FIG. 2.

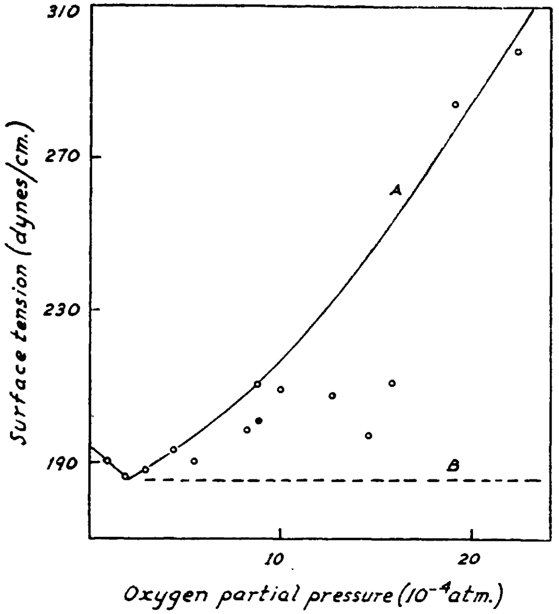
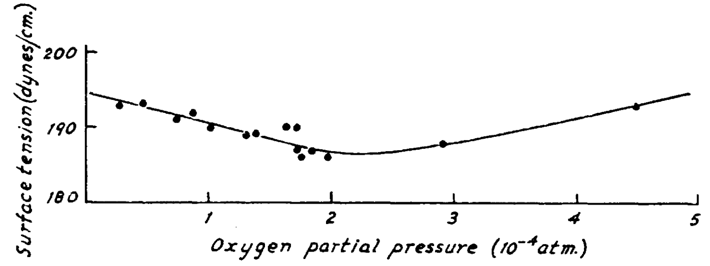


FIG. 3.



In each determination, the sodium was allowed to flow from the pipette into a pure argon atmosphere until the flow rate was steady. Since the head of pressure in the pipette falls, steady flow is shown by a regular increase in drop time (line *a*, Fig. 1). When these conditions were achieved, contaminated argon was introduced; increase or decrease in surface tension is revealed by a corresponding increase or decrease in time of formation of the drops. The measurements shown in Fig. 1 are typical of those obtained on introduction of a very small quantity of air into the argon stream. Since a short time is required for the oxygen content of the argon surrounding the orifice to reach its final value, drop times did not undergo full adjustment immediately, but within the period for 3—4 drops, the drop times moved from line *a* to a line *b* which is nearly parallel with *a*. Lines *a* and *b* are of course short sections from curves which are not parallel, and drop volumes were therefore calculated from drop times t_1 and t_2 determined as shown in Fig. 1. When the difference between t_1 and t_2 was considerable, tensions were calculated by using the usual equation $\gamma = mgF/r$. This was the case only with the most heavily contaminated surfaces, and for most experiments the variation in correction factor F was so small that the tension of the contaminated surface could be obtained with sufficient accuracy by using the simple relation $\gamma = \gamma_{Na}t_1/t_2$.

RESULTS AND DISCUSSION

The variation in surface tension at 180° with oxygen partial pressure (over the low partial-pressure range) is shown in Fig. 3, from which it is at once apparent that the presence of oxygen at first causes lowering of the surface tension, but that slight surface contamination does not have any marked effect on the measured tension values. At an oxygen partial pressure of about 2×10^{-4} atm. the tension value passes through a minimum, and increases thereafter. When the quantity of oxygen was less than about 2×10^{-4} atm., the drops normally remained bright, whereas with higher oxygen partial pressures, films of undissolved oxide were visible. The appearance of undissolved oxide on the surface therefore broadly coincided with the minimum in the surface-tension curve; the initial decrease in tension from 194 to 186 dynes/cm. results from a soluble film of sodium oxide, and the fact that the decrease is only 8 dynes/cm. is a consequence of the very low solubility of sodium oxide. It is of interest that the tension value of 186 dynes/cm. at 180° obtained by the vertical plate technique (Part I, *J.*, 1954, 2861), in which the sodium surface is exposed for longer periods, agrees with the minimum value observed in these experiments (Fig. 3), so that the range of values for the tension of " pure " sodium obtained by the various techniques is also that for which sodium oxide can be responsible.

At oxygen partial pressures beyond the minimum in the tension curve, an insoluble oxide film is formed, and the cohesion in this film is responsible for the increase in the apparent surface tension. The behaviour of the drops under these conditions was erratic. When the oxide film remained unbroken throughout drop formation, maximum values of tension (representing the sum of the true sodium tension and the film cohesion) were obtained, and these conditions are represented by curve *A*, Fig. 2, which could be extended to tensions as high as 450 dynes/cm. Frequently, however, the film cracked, exposing clean sodium metal, and lower tension values were then obtained. According to the general hypothesis all values should lie between curve *A* (maximum film cohesion) and line *B* (no film cohesion); this was the case, and no values were obtained below line *B*. This interpretation is consistent with observations by Moyer and Ruggles (Knolls Atomic Power Laboratory Report KAPL-519, May 1951) who studied the optical properties of a liquid sodium surface by reflection of plane-polarised light from the surface. They found that small quantities of oxygen in a helium atmosphere dissolved in the liquid metal without change in the optical characteristics of the surface, but that addition of oxygen in excess of the solubility limit gave rise to clumps of oxide crystals, the space between the crystals being covered with a thin oxide film.

The results in Fig. 3 show that reaction between sodium and dry air is very slow, since sufficient oxygen was available at all times to give rise to heavy contamination of the drops. It is, indeed, only in such circumstances that measurements of the type shown in Fig. 3 are possible. Using a solid sodium surface, Moyer and Ruggles (*loc. cit.*) found that 10—15 days were required before reaction with traces of oxygen in a helium atmosphere was complete. Their observation that small amounts of nitrogen sensitised the surface so that the oxygen was taken up in less than a second is also of interest; nitrogen was present in the experiments described here, and may be responsible for some increase in reaction rate, but its catalytic activity at the liquid-metal surface appears to be much less than at the solid surface. The results serve to establish the general influence of oxygen on surface tension, but the Gibbs absorption isotherm cannot be applied to the falling tension curve (Fig. 3) since equilibrium is not established under the conditions of these experiments. For this reason also, variation in the rate of drop formation (between 15 and 75 seconds per drop) had little effect on the tension values. Reaction at the surface is believed to follow the form

$$Na + O_2 \longrightarrow NaO_2 \xrightarrow{Na} Na_2O_2 \xrightarrow{Na} Na_2O$$

Although dissolved oxygen is no doubt present as sodium monoxide, an insoluble film may well contain sodium peroxide, since this compound is not readily wetted by sodium. The sodium–oxygen reaction is much more rapid in the presence of moisture; the decrease in tension with oxygen content is then likely to be more rapid than in Fig. 3, and the values may also depend to some extent on rate of drop formation. However, since systems to which the present measurements are relevant are scrupulously dried, this aspect was not further investigated.

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