Liquid Metals. Part I. The Surface Tension of Liquid Sodium : the Vertical-plate Technique.

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This paper describes the determination of the surface tension of liquid sodium in an atmosphere of pure argon, from measurements on plates of zinc, copper, and molybdenum suspended, and partly immersed, in liquid sodium. In the temperature range 100—200° zinc can be fully wetted by sodium, but copper and molybdenum are not wetted; the technique employed for contact angles of 0° and 180° is described. The surface tension is found to be 195 dynes/cm. at the melting point, and the temperature coeffiicent is 0·1 dyne/cm./degree.

The study of surface properties in liquid-metal systems is rendered difficult by the ready formation of contaminating films on the metal surface. With the liquid alkali metals, considerable precautions are necessary to prevent the formation of oxide films, and in consequence the earlier values reported for the surface tension of liquid sodium show a wide scatter. The first determination (252 dynes/cm. at the melting point) was made by Quincke (*Ann. Physik*, 1868, **135**, 621) using the drop-weight method and an atmosphere of carbon dioxide. Poindexter and Kernaghan (*Phys. Review*, 1929, **33**, 834) measured a sessile drop of sodium in a vacuum, and obtained a value of 206·4 dynes/cm. at 103°. By use of the capillary-rise technique, values in the range 110—125 dynes/cm. have been reported ("Liquid Metals Handbook," 2nd Edn., NAVEXOS P-733, Rev., p. 53, U.S. Govt. Printing Office, Washington D.C., 1952) but the fact that the value varied with the material used to contain the sodium illustrates the unsatisfactory nature of the results.

The main objective of the present work is the study of the wetting of solid metals by liquid metals, and the influence on contact angles of such factors as temperature, atomic structure of the metal, physical state of the surface, and oxide films. The technique now described was originally designed for contact-angle measurements; a plate of the solid metal is partly immersed in the liquid metal, and the force on the plate is dependent upon (*inter alia*) the surface tension of the liquid metal and the contact angle. A knowledge of the surface tension is therefore essential for contact-angle measurements; however, by suitable selection of the solid metal it has been possible to define conditions under which the contact angle is either 0° or 180°, and the apparatus may then be used for the measurement of surface tensions of liquid metals.

EXPERIMENTAL

Vertical-plate Apparatus.—The apparatus is shown diagrammatically in Figs. 1*a* and 1*b*. The torsion device was housed in a brass box 25 × 21 × 15 cm. (shown in broken outline in Fig. 1*b*) through which argon was normally circulated *via* openings at *C* and *D*. The whole apparatus could be evacuated if desired. *AB* was a stainless-steel torsion wire 0·0406 cm. in diameter and 18 cm. long, free from fatigue. It was held firmly at *A* and *B* in chucks which were inserted, through lock-nuts, into Wilson seals set into the walls of the box. These seals allowed the chucks to be turned, but prevented ingress of air. *A* was normally maintained in a fixed position, while *B* was attached to the pointer *P* on the outside of the box (Fig. 1*a*). *E* was a light aluminium arm 13 cm. long (V-shaped to prevent bending) which was clamped rigidly to the torsion wire by block *F*. The vertical plate was suspended from the end of arm *E* by nichrome wire (diam. 0·051 cm.); this wire was looped through a hole in the end of arm *E* only slightly greater in diameter than the wire, so that the wire was free to move in a vertical plane. The weight of the arm, the plate, and its suspension wire was approximately counterbalanced by a weight suspended as shown on the opposite side of block *F*. The movement of the vertical plate (and thus arm *E*) was followed by an optical lever system. A concave mirror *M* of long focal length was mounted on *F*, and a spot-light and hair-line were reflected, through the glass window

W, on to a circular scale *S* having its centre at *M*, and of about 1 m. radius. The position of the vertical plate with respect to the liquid sodium surface was controlled by movement of pointer *P*. The characteristics of the torsion wire were such that the movement of *P* through an angle of 180° caused a vertical displacement of the plate (when hanging free) of about 7 cm. Calibration curves from which the force on the plate could be obtained from the setting of pointer *P* and the scale reading were derived as follows. The plate was allowed to hang freely (*i.e.*, in the absence of liquid sodium) and the scale reading corresponding to a particular setting of *P* was noted; a series of known weights were then suspended on the plate, and a force–scale reading graph obtained. This was repeated for a range of pointer settings, the calibration curves being determined when the apparatus was at the temperature at which the tension measurement was to be carried out.

The plate suspension wire passed out of the brass box down the centre of a brass tube 3·2 cm. in diameter, which was attached by a metal vacuum union *G* to the glass system. The vessel *K* in which the plate was suspended carried a B.55 ground-glass joint, and was 10 cm. in diameter. This was sufficiently wide to ensure that when the vessel contained sodium, the plate was immersed in a plane surface, and that the measurements were not influenced by sodium–glass meniscus effects. Vessel *K* carried a side arm in which a micrometer *H* (containing a silicone rubber vacuum seal) and a probe were attached. This was used to detect any change in the sodium level during an experiment. In conjunction with a cathetometer it could also be used to determine the depth of immersion of the plate, although this depth was more conveniently obtained directly from readings on scale *S*.

FIG. 1*a*.

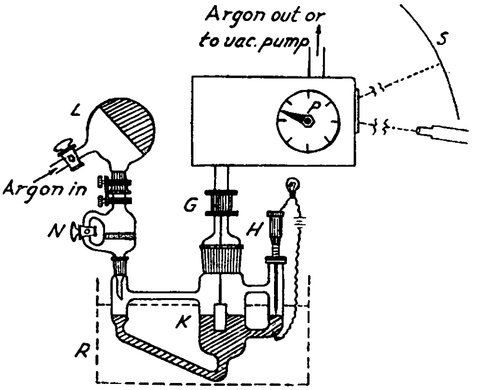
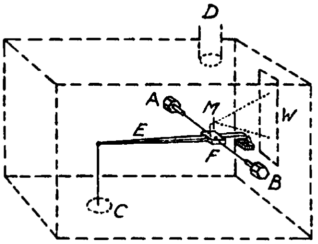


FIG. 1*b*.



Method.—The experiment was carried out as follows. The sodium (which had been given preliminary purification as described below) was contained in vessel *L*; *L* was attached, by a B.24 ground-glass joint, to the filtration unit *N* which contained a Grade 3 sintered-glass plate 7 cm. in diameter. The joint was held by a metal clip in order to withstand the pressure of argon gas necessary during filtration. The filtration unit was connected to vessel *K* through a B.14 joint as shown. The apparatus was first evacuated; vessels *N* and *K* were heated (by Electrothermal heating tapes) to a temperature about 100° above that of the experiment, in order to degas the glass. Purified argon gas was then allowed to flow through the apparatus at a rate of about 1 l./min. The oil thermostat *R* was raised into position, and the filter unit *N* and the vessel *L* were heated to 120° by wrapping them with heating tapes. During this stage the tap *N* was kept open. The sodium in *L* melted, and flowed on to the sintered plate; when 40—50 ml. had collected on the plate, tap *N* was closed, and the sodium forced through the plate into vessel *K* by argon pressure. This process was repeated until *K* contained the necessary quantity of sodium (normally about 150 ml.), whereupon tap *N* was left open and vessel *L* allowed to cool. The plate was lowered until it touched the sodium surface, and the scale reading noted. The procedure followed thereafter depended upon whether the plate was wetted by sodium.

(a) *Zinc plates.* The influence of surface condition of the zinc on rates of wetting will be discussed in a later paper. For plates prepared as described below, wetting was almost immediate. The plate was immersed to a depth of 2—3 cm. and then gradually withdrawn. The scale readings corresponding to a series of settings of the pointer P were noted, and the corresponding force on the plate used in the calculation of surface tension.

(b) *Copper and molybdenum plates.* Wetting did not occur with these plates within the temperature range employed. The plate was pressed into the surface, and scale readings noted for a series of pointer settings. The depth of immersion of unwetted plates was limited; as soon as the plate was immersed beyond the floating position, it moved to the side of vessel K, preventing further measurement.

Depth of immersion of the plate. This was determined from the scale readings when the plate touched the surface (S_s) and when immersed to depth l (S_l). From the geometry of the apparatus, $l = 0{\cdot}0682(S_l - S_s)$ cm.

Correction for sodium wetting the zinc plate. It was necessary to subtract the weight of the sodium film from the measured force in the suspension wire. This was done by selecting an appropriate pointer setting, and noting the change in scale reading for the freely hanging plate before immersion in, and after removal from, sodium. From this change, the calibration curves gave the weight of sodium wetting the full area of plate which had been immersed. Jeffreys (*Proc. Camb. Phil. Soc.*, 1930, **26**, 204) derived the relation $z^2 = \eta y/gt_1$ between the thickness of film z and the distance y below the wetted edge, for a liquid draining from a vertical surface with zero contact angle; η is the kinematic viscosity and t_1 the time of draining. This equation being applied to the plates used, the weights of sodium wetting the plate are 0·009, 0·007, and 0·005 g. for draining times of 5, 10, and 20 sec., respectively. The equation is based on considerations of liquid flow only, and the direct measurements referred to above showed that the weight of sodium retained was near 0·034 g. in all experiments with plates of standard size. Since drainage times longer than the above were normally used, there remains 0·03 g. of sodium which must be adhering to the plate as an intermetallic compound (*e.g.*, $NaZn_{12}$: Mathewson, *Z. anorg. Chem.*, 1906, **48**, 196). This compound does not dissolve in sodium, and must decompose in water to leave the zinc on the plate, since the weight of the plate after being immersed in sodium and cleaned by washing with water and drying with alcohol and ether, differed from the weight of the original plate by less than 0·001 g. This weight of combined sodium was used as a constant correction, to be added to the weight of the plate irrespective of the immersion depth. This procedure assumes that the dimensions of the plate are not altered by this combined sodium; if this is not so, then a slight correction should also be made to the buoyancy term $txdl$ in equation (1) (p. 2864). That this latter correction is unnecessary is indicated by the constancy of the tension values for a range of immersion depths. Again, it has no bearing on the final tension value, since the buoyancy term becomes less significant as the plate is withdrawn from the liquid.

No such corrections were necessary with the copper and molybdenum plates, which showed no change in weight after immersion in sodium.

Preparation of Plates.—The plates measured approximately 5 × 2 × 0·06 cm. Molybdenum plates were abraded with emery paper of grades 1 to 4/0, and then degreased in a Soxhlet extractor with dry acetone for 12 hr. The plate was removed from the acetone, and dried rapidly in a current of warm air, immediately before use in a tension measurement. Some zinc plates were prepared similarly, and some were electropolished in an orthophosphoric acid bath prepared as described by Jacquet (*Métaux Corrosion Usure*, 1944, **19**, 71), a current density of 2·2 amp./sq. dm. and 2·5 volts being used. Copper plates were electropolished in orthophosphoric acid (d 1·4) at 2·0 amp./sq. dm. and 2·2 volts, a copper cathode being used.

Density of Sodium.—The values used in calculation were those given by Ewing, Atkinson, and Rice (N.R.L. Report C.3287, 1948) which conform to the equation $d = 0{\cdot}957 - 2{\cdot}7 \times 10^{-4}T$.

Purification of sodium. The sodium used was supplied by British Drug Houses Ltd.; the maximum content of other metals is as follows; Ca, 0·069; Fe, 0·0007; Mn, 0·0001; Ni, 0·00005; Cu, 0·0002; Pb, 0·0003%. The impurity which has the greatest influence on surface properties, and which is most difficult to remove, is oxygen (present as Na_2O). Sodium monoxide has an exceedingly low solubility in liquid sodium. Direct measurements (collected references in "Liquid Metals Handbook," *op. cit.*, p. 114) have shown the solubility to be less than 0·002% over the temperature range used in this work. As an alternative to distillation, Bornemann (*Z. angew. Chem.*, 1922, **35**, 227) has described the removal of oxide by filtration through sintered stainless-steel plates. This gives liquid sodium containing little more than the oxide dissolved at the temperature of filtration. We have found sintered-glass plates to be very successful for oxide removal, and the fact that the surface tension of sodium so purified agrees closely with values determined by Taylor (A.E.R.E. Report M/R 1247, 1953) on carefully distilled sodium supports this. Although sodium metal does not wet glass, sodium monoxide adheres strongly to glass, and the oxide in excess of that dissolved can therefore be removed by bringing liquid sodium into contact with a sufficient area of glass surface. This was achieved by the passage of sodium through the sintered-glass plate in unit *N* (Fig. 1*a*). The function of this plate was not filtration as normally understood; instead it provides a means of finely subdividing the sodium, and thus bringing it into intimate contact with a large area of glass surface.

The sodium was given a preliminary filtration through glass-wool to remove the main bulk of oxide and carbonate. It was then solidified, cut in an argon-filled dry box, and transferred to a vertical glass tube 4 cm. in diam. and 50 cm. long. This tube carried a constriction near the bottom, on which rested a 5-cm. plug of cleaned glass-wool. Argon was led into the top of the tube, and the round-bottomed flask shown as *L* in Fig. 1*a* was attached at the bottom. The tube was wrapped with heating tapes and warmed to about 100°, and the main proportion of the volatile contaminants carried away in a stream of argon. The temperature was then raised to 150°, the sodium flowing through the glass-wool plug into flask *L*. This flask was then isolated in a stream of argon, attached to a high-vacuum line, and gaseous impurities were removed from the sodium by heating for 5 hr. at $250°/10^{-5}$ mm. The metal was then allowed to solidify, and the flask transferred to the position shown in Fig. 1*a*. The temperature of final filtration through the plate *N* was kept as low as possible; although the temperature coefficient of solubility of sodium monoxide is small at temperatures up to 250°, it was observed in early experiments that low values of tension resulted when the sodium was filtered at a temperature above that used for the tension measurement.

Purification of Argon.—Argon of the highest purity was necessary to prevent surface contamination of the sodium. The argon used (British Oxygen Co. Ltd.) was 99·8% pure. This was further purified by passage through fresh calcium metal chips heated to 700°, and then through stainless-steel bubblers containing sodium–potassium alloy.

RESULTS AND DISCUSSION

When a metal plate is suspended and partly immersed in liquid sodium, the equilibrium state is expressed by the equation

$$\gamma \cos \theta = g[txdl + (F - W)]/2(t + x) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the surface tension of sodium, θ is the contact angle, *t*, *x*, and *W* are the thickness, width, and weight of the plate, *l* is the depth of immersion of the plate, *d* is the density of sodium, and *F* is the force (in grams weight) exerted by the suspension wire. This relation may be employed to determine either γ or θ provided that the other is known. The manner in which $\gamma \cos \theta$ varies as the depth of immersion of a zinc plate is decreased is shown in Fig. 2; γ is constant, and the initial rapid increase in $\gamma \cos \theta$ reflects the decrease in receding

TABLE 1.

Surface age of sodium = 110 min. Electropolished zinc plate. Temp. = 176°. "Wetted plate" correction = 0·030 g.

$t = 0{\cdot}051$ cm. $x = 2{\cdot}06$ cm. $W = 2{\cdot}861$ g. $d = 0{\cdot}910$ g./c.c. $S_s = +3{\cdot}55$.

Pointer setting	S_t	Immersion depth, *l* cm.	*txdl* (g.)	$F - W$ (g.)	$\gamma \cos \theta$ (dynes/cm.)
80°	40·3	2·51	0·240	0·405	143
90	37·5	2·38	0·203	0·593	182
100	27·6	1·64	0·157	0·678	187
110	17·1	0·94	0·090	0·752	188
115	10·3	0·46	0·044	0·783	185
120	4·5	0·06	0·006	0·825	186

TABLE 2

Expt. No.	Dynes/ cm.	Metal plate	Expt. No.	Dynes/ cm.	Metal plate	Expt. No.	Dynes/ cm.	Metal plate
1	186	Abraded zinc	6	187	Abraded zinc	11	186	Electropolished zinc
2	185	,,	7	186	,,	12	189	,,
3	185	,,	8	186	,,	13	187	Copper
4	186	,,	9	186	,,	(170°)		
5	187	,,	10	183	Electropolished zinc	14	186	Molybdenum

contact angle. When θ reaches 0° the curve changes direction, and thereafter $\gamma \cos \theta$ ($= \gamma$) is constant. With copper and molybdenum plates, the value of $-\gamma \cos \theta$ increases rapidly as the plate is forced into the surface. When the advancing angle θ reaches 180° the curve changes direction sharply, and $-\gamma \cos \theta$ ($= \gamma$) is constant throughout further immersion of the plate. The detailed results of one typical experiment are given in Table 1, in order to illustrate the relative magnitude of the terms in equation (1).

A series of such determinations has been carried out and Table 2 gives the γ values obtained at or near 180°. Errors in measurement are considered to lead to an experimental error of ± 1 dyne/cm., and the results are therefore reported to the nearest dyne. The mean of these values gives the surface tension of sodium as 186 dynes/cm. at 180°.

Temperature Coefficient of Tension.—By using an abraded zinc plate, values of the surface tension have been determined over the temperature range 128—180°, and are shown in Fig. 3. A number of metals show a " critical wetting temperature " above which wetting by sodium is a ready process, but below which wetting occurs with difficulty, if at all. This property will form the subject of a later paper, but it is relevant that the critical wetting temperature for zinc falls within the temperature range used. When the zinc plate was immersed in sodium at 128°, the contact angle remained large and the tension could not be determined. However, when the plate was wetted at 180°, and the sodium then cooled below the critical wetting temperature, the contact angle remained at zero; this technique was used where necessary in obtaining the tension values shown in Fig. 3. The temperature coefficient is $-0{\cdot}1$ dyne/cm. degree^{-1}, and extrapolation gives $\gamma = 195$ dynes/cm. at the m. p. of sodium. These results are in quite good agreement with values recently obtained by Taylor (*loc. cit.*) using the maximum bubble pressure method; the temperature coefficient is in each case the same, and is in good agreement with a value $-0{\cdot}09$ dyne/cm. degree^{-1} calculated by Skapski (*J. Chem. Phys.*, 1948, **16**, 386).

FIG. 2.

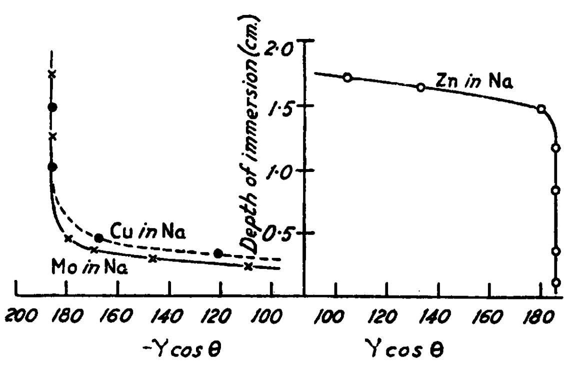
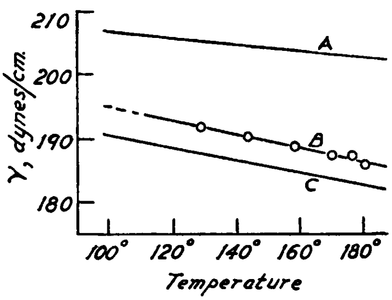


FIG. 3.



A, from results of Poindexter and Kernaghan (*loc. cit.*)
B, present work.
C, from results of Taylor (*loc. cit.*).

Influence of Surface Films of Sodium Oxide.—Taylor (*loc. cit.*) finds $\gamma = 191$ dynes/cm. at the m. p.; a difference of 4 dynes/cm. is not, in fact, likely to represent any real disagreement in view of the corrections necessary in the two widely different techniques. In Taylor's measurements great care was also taken to avoid contamination of the sodium surface by oxide, but since there is always the possibility, with strongly electropositive metals, that slight contamination may occur, it is necessary to consider the influence of oxide films on surface tension. The surface tension of fused metal oxides is normally much lower than that of the corresponding liquid metals (see Bondi, *Chem. Rev.*, 1953, **52**, 417). Consistently with this, sodium oxides are not wetted by liquid sodium, since the condition $\gamma_{\text{solid}} > \gamma_{\text{liquid}}$ is desirable before wetting takes place. Provided that the oxide content of the metal is below the solubility limit, its presence in the surface will almost certainly lower the tension of the liquid metal. When sufficient oxide is present at the surface to form an insoluble film, the effect on tension depends upon the cohesive nature of the oxide concerned.

Sodium oxide films are strongly cohesive, and increase the apparent surface tension. In measurements on sodium using the drop-weight method, apparent values of surface tension as high as 300 dynes/cm. were observed when the drops carried a visible film of oxide. Therefore the effect of sodium oxide at the surface is first to lower the tension, and then to increase it. There appears to be no justification, however, for the assumption that the higher tension values reported by Poindexter and Kernaghan (*loc. cit.*), and shown in Fig. 3, arise from oxide contamination of the sessile drop, although the temperature coefficient, 0·05 dyne/cm. degree^{-1}, is unusually low for a metallic element. These measurements were carried out in a high vacuum, and may well represent the true surface tension of sodium under these conditions. It is well known (*e.g.*, with mercury) that the presence of adsorbed gases or vapours can lower the surface tension of liquid metals.

Variation of Surface Tension with Time.—The measurements referred to in Table 2 were normally continued for periods of 2—3 hr. In many cases no change in tension took place during this time. Occasionally, a slight fall in tension occurred after one hour, but this did not exceed 2 dynes/cm. The slight decrease is attributed to oxide contamination, since argon flowed over the metal surface throughout the experiment.

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