228. *Liquid Metals. Part VIII.*[1] *The Surface Tensions of Liquid Barium and Liquid Calcium.*

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The paper reports the first measurements of the surface tensions of liquid barium and liquid calcium. The maximum-bubble-pressure method has been used, with highly purified argon as the blanket and the bubble gas. The temperature range extends from the melting points (Ba, 720°; Ca, 850°) to about 1000°. The surface tensions (γ) are expressed by the equations: liquid barium, $\gamma = 292 - 0{\cdot}095t$; liquid calcium, $\gamma = 395 - 0{\cdot}068t$; where t is in degrees Centigrade. The surface tensions at the melting points are 224 and 337 dynes/cm., respectively. Liquid barium behaves quite normally, but liquid calcium possesses a number of unusual physical properties which are here described.

A KNOWLEDGE of the surface tensions of liquid barium and liquid calcium became necessary in order to assess the extent to which the solutions of these metals in liquid sodium (Part VI [2]) conform to ideal behaviour. These solutions, in turn, are of interest because their ability to wet the transition metals is very different from that of pure liquid sodium (Part V [3]). The results should also be of value in connection with various attempts now being made to correlate the physical properties of liquid metals. Partly because of the extreme experimental difficulties encountered in measuring the surface tensions of reactive liquid metals at high temperatures, there has been continued interest in theoretical relations between surface tension and other physical constants; given a generally applicable correlation, it might then be possible to calculate surface tensions from some property which is more easily measured. To date, however, such attempts have been hindered by the limited amount of experimental data, and magnesium [4] is the only Group II metal for which surface-tension values are recorded.

Using correlations with the various physical properties listed in Table 1, Taylor [5] has estimated the surface tensions of liquid barium and calcium, but the values obtained bear little relation to one another.

TABLE 1.

Estimated values of surface tensions [5] of liquid barium and liquid calcium at their melting points.

Properties correlated	Estimated γ (dynes/cm.) for: liquid Ba	liquid Ca
Surface tension–atomic vol.	70	160
,, ,, heat of sublmn.	190	250
Excess surface binding energy–heat of sublmn.	200	260
Surface tension–m. p.–atomic vol.	430	560
,, ,, density–elastic modulus	390	610

In addition, Zadumkin [6] reported two estimated values for liquid calcium of 342 and 360 dynes/cm. at 1240°, and compared them with "experimental" values of 353 and 358 dynes/cm. In neither case, however, is reference given to the source of the data, the method of measurement, the temperature, or the metal purity. Grosse [7] has recently attempted a correlation between the surface tensions and the critical temperatures of

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[1] Part VII, Addison and Pulham, *J.*, 1962, 3873.
[2] Part VI, Addison, Coldrey, and Halstead, *J.*, 1962, 3868.
[3] Part V, Addison, Iberson, and Manning, *J.*, 1962, 2699.
[4] Liquid Metals Handbook, 2nd edn., NAVEXOS–P. 733, U.S. Govt. Printing Office, Washington, 1952.
[5] Taylor, A.E.R.E. Report M/TN.25, 1954; *Metallurgia*, 1954, **50**, 161.
[6] Zadumkin, *Doklady Akad. Nauk, S.S.S.R.*, 1953, **92**, 115; *Zhur. fiz. Khim.*, 1955, **27**, 502.
[7] Grosse, *J. Inorg. Nuclear Chem.*, 1962, **24**, 147; 1961, **22**, 23, 333.

liquid metals, but zinc, cadmium, and mercury lie outside the broad correlation found for a number of other metals. It is clear, therefore, that all such correlations are at present highly speculative and provide no substitute for direct measurement of surface tension.

EXPERIMENTAL

The purity and cleansing of the metals has already been described.[1,2] The barium and calcium used melted at 720° and 850°, respectively. Surface tensions were measured by the maximum-bubble-pressure method, with argon as the blanket gas and for bubble formation. The furnace assembly is shown in Fig. 1. The furnace itself, and the temperature control (±2°), resemble those used in the determination of the density of liquid barium [1] and need not be described further. A stainless-steel capillary tube A entered the lid of the furnace through a Sindanyo collar B, which allowed vertical movement of tube A. The end of tube A was turned on a lathe to form a knife edge orifice. Orifice radii were of the order of 1—2 mm.; the values employed in calculation were mean values from 20 measurements of the radius. The depth of immersion of the orifice below the liquid-metal surface was measured from the position of a calibration mark on tube A with respect to the scale F. Originally, several calibrated screw mechanisms for raising or lowering tube A were tested, but at furnace temperatures near 1000° these jammed as a result of expansion. Scale F was therefore mounted rigidly on the furnace lid and tube A was moved by hand. Silicone tubing was used for all flexible connections to the furnace assembly.

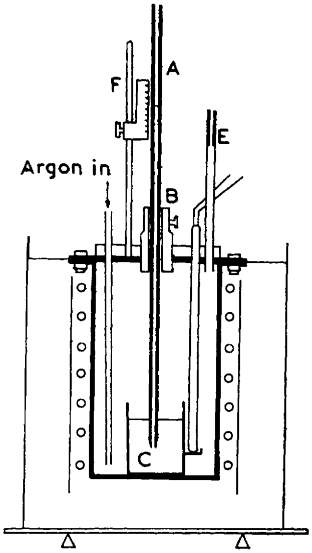

FIG. 1. Apparatus for the determination of the surface tensions of liquid barium and liquid calcium. (For key see text.)

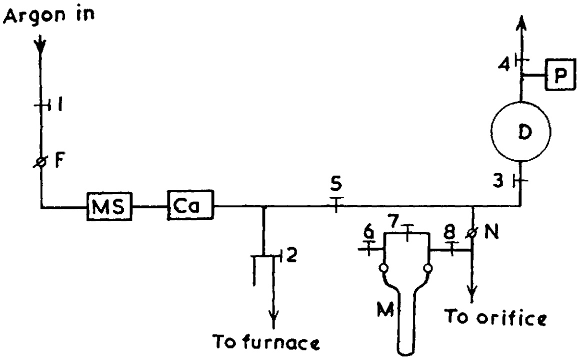

FIG. 2. Argon supply system.

Argon Supply System.—The need for very pure argon has already been emphasised.[1] The gas system used is shown schematically in Fig. 2. Argon (British Oxygen Co., 99·95%) was metered at a rate of 1—2 l./min. by tap 1 and flowmeter F through the purifying system, consisting of calcium chips at 600° (to remove oxygen, nitrogen, etc.) and molecular sieve (MS) (to remove water). For use as a blanket gas in the furnace, argon then passed through the two-way tap 2, which also served as an outlet to the atmosphere when required. A controlled flow of argon to the orifice was obtained by using a 1-l. reservoir D and pressure gauge P placed between taps 3 and 4, and at an excess argon pressure of about 10 cm. Hg. This part of the system could be isolated by tap 5 from the blanket-gas flow, and the needle valve N gave a possible variation in bubble rates from 0·2 to 120 sec. per bubble. Bubble pressures were read from manometer M with an accuracy of 10^{-3} cm., and the temperature at the manometer was checked continuously throughout an experiment.

Procedure.—(*a*) *Barium.* About 200 g. of barium were placed in the steel beaker C (Fig. 1) under a pure argon atmosphere. The apparatus was then assembled and flushed with pure argon for an hour, with all taps open. When the furnace temperature was steady, tap 4 (Fig. 2) was closed, the gas pressure in reservoir D (Fig. 2) was increased, and taps 1 and 5 and the needle valve N were closed. The position of the orifice was then adjusted to the surface of the liquid barium by observation of the manometer M. Thus, tap 7 was closed, tap 8 opened, and the needle valve then opened very slightly; the only gas flow to the furnace was then the gas flowing out of the orifice from reservoir D. As the capillary tube A was lowered, the pressure in M rose perceptibly when the orifice was sufficiently near the liquid-metal surface to restrict the flow of gas. Further slight lowering of tube A resulted in contact with the liquid surface, and the pressure in M rose sharply as bubbles formed. At bubble rates slower than 3—4 sec. per bubble, the maximum pressure ($P_{\text{max.}}$) was independent of bubble rate; for all measurements on barium a standard rate of 7 sec. per bubble was used. The above procedure was then repeated for various depths of immersion of the orifice.

In calculating the results, corrections were applied for (1) expansion of the orifice, (2) variation in level of the liquid barium due to immersion of the orifice, and (3) gravitational distortion of the bubble from a hemisphere (Sugden's method [8]).

(*b*) *Calcium.* The procedure was essentially the same as for liquid barium, but liquid calcium presented several additional difficulties. It appears to have a higher vapour pressure than barium when molten, and the vapour carried out by the argon stream from the exit tube E (Fig. 1) formed white fumes of calcium oxide on contact with the atmosphere outside the furnace. A small concave flame burned at this outlet and the appearance of the flame coincided with the melting of the metal. At high rates of argon flow, particles of condensing calcium were ejected as sparks from the exit tube. (Vapour-pressure measurements have been made on solid calcium,[9] but not on the liquid.) As a result of this, the argon outlet tube tended to become choked with calcium oxide whatever its length. To overcome this, the argon flow to the furnace was stopped as soon as the apparatus was ready for measurements, and the outlet tube E (Fig. 1) was joined to tap 6 on the manometer (Fig. 2) by wide-bore Silicone rubber tubing. In this way the manometer recorded the true pressure required for bubble formation even though a slight positive pressure may have been generated in the furnace.

RESULTS AND DISCUSSION

Liquid Barium.—The surface tensions of liquid barium from the melting point (720°) to 1000° are recorded in Table 2. Values for the density of liquid barium used in the calculations were those already determined in these laboratories.[1]

Fresh barium metal, orifice tube, and containing beaker were used for each experiment.

TABLE 2.

Surface tension of liquid barium.

Orifice radius (cm.)	Depth of immersion (cm.)	Temp.	Surface tension (dynes/cm.)	Orifice radius (cm.)	Depth of immersion (cm.)	Temp.	Surface tension (dynes/cm.)
	Stainless-steel beaker				*Pure iron beaker*		
0·124	0·0	720°	226	0·169	0·0	720°	226
	1·53	755	222		1·02	721	224
	1·53	780	221		2·04	721	221
	1·02	859	208		1·02	771	212
	1·02	875	203		0·0	817	215
	1·02	880	210				
				0·181	0·0	935	206
0·121	0·0	1003	199		0·0	936	206
					0·0	946	206

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[8] Sugden, *J.*, 1922, 858.

[9] Tomlin, *Proc. Phys. Soc.*, 1954, **67**, 781.

When plotted, the results lie close to a straight line, and the method of least squares gives the relation between surface tension (γ) and temperature t (°c) as:

$$\gamma = 292 - 0{\cdot}095t$$

The surface tension at the melting point, 720°, is 224 dynes/cm. All measurements recorded in Table 2 were completed within an hour of melting the barium. Within this time bubble formation was ideal; the small scatter in the results is to be attributed to manipulative difficulties at temperatures at which the centre of the furnace was well above red heat, and in particular the exact determination of the liquid surface level. In contrast to calcium, the behaviour of barium was generally very satisfactory; the results show no systematic variation with orifice radius or depth of immersion of the orifice. Results obtained in steel or pure iron beakers are consistent, so that no significant attack takes place during the first hour. Both iron and stainless steel are completely wetted by liquid barium; this was verified by touching the surface with the orifice and then raising it 0·12 cm. above the surface level; bubbles could then still be blown in the liquid.

Some experiments were continued for longer periods to examine the behaviour of the system on prolonged contact. After about one hour, $P_{\text{max.}}$ slowly decreased with time. Dismantling the apparatus after several hours showed a deposit of solid metal which was presumably a barium–iron alloy (together with barium–nickel alloy in the case of stainless steel) on the immersed part of the orifice tube, so that bubble formation was occurring from an orifice of increasing radius. This effect was scarcely observable after 1·5 hours, but after 4 hours' immersion the diameter of the orifice tube had increased to almost twice its original size. The alloy was removed by washing with water, and both orifice tube and beaker were seen to be etched, particularly at the barium–argon surface. Analysis of barium which had been molten for 4 hours in a stainless-steel beaker gave 0·05% of iron and 0·02% of nickel. Reaction of pure iron with liquid barium is only slightly greater than that of stainless steel.

Liquid Calcium.—Calcium possesses a number of physical and chemical properties which render the determination of surface tension much more difficult than in the case of liquid barium.

Formation of calcium nitride. Calcium reacts readily with nitrogen at elevated temperature, and especially in the liquid and the vapour state. In one experiment in which the argon (99·95%) was dried through a molecular sieve but from which nitrogen was not removed, a large proportion of the liquid calcium was converted into the red-purple Ca_3N_2 which was deposited on the inner walls of the furnace.

" Creeping " of liquid calcium. Liquid calcium shows a marked ability to creep up the walls of the containing vessel and orifice tube. This we attribute in part to the high ΔG value for the formation of calcium oxide ($\Delta G_{298} = -143$ kcal./mole) which enables the metal to reduce the thin (~50 Å) film of iron, chromium, or nickel oxide on the surface of the steel beaker. It will then wet the unprotected transition metal, and this will lead to a climbing film of calcium metal. This film was able to reach the rim of the beaker and continue down the outside. If the argon was scrupulously pure, liquid calcium was thus able to flow from the inside to the outside of the containing beaker. Any traces of nitrogen impurity in the argon reacted with this film, producing a brittle mass of calcium and calcium nitride on the rim of the beaker; when this was dissolved in water, ammonia was produced but no iron hydroxide was precipitated. These observations emphasised the need to complete measurements in the shortest possible time. The values reported in Fig. 3 were obtained within 15 minutes of melting the calcium.

Behaviour of bubbles in liquid calcium. As with liquid barium, the value of $P_{\text{max.}}$ increased as bubble rate slowed to 3—4 sec. per bubble, and was substantially constant at slower bubble rates. In contrast to barium, however, the pressure readings then became more irregular as bubble rate was reduced. Measurements were, therefore, made at a standard rate of 4 sec. per bubble. At this rate, $P_{\text{max.}}$ normally remained constant throughout a measurement at a value corresponding to a surface tension of about 330 dynes/cm. (Fig. 3). In several instances, however, an initial $P_{\text{max.}}$ value corresponding to a surface tension of about 270 dynes/cm. was maintained for about 2 minutes, after which $P_{\text{max.}}$ rose sharply to the higher value and remained there throughout the remainder of the experiment. There are clearly some unusual orifice phenomena associated with liquid calcium which were not observed with barium; isolated experiments may give false results, and it is for this reason that a larger number of determinations have been carried out on liquid calcium.

Containing vessels. After Culpin's observations[10] that graphite was resistant to liquid calcium at 900° and that there was no evidence of carbide formation, a graphite crucible was first tested as a container. However, the calcium permeated into the graphite and this was therefore abandoned in favour of stainless steel, which was only slightly attacked (calcium which had been molten for several hours at 1000° was chilled suddenly to avoid separation of any dissolved metals; analysis gave 0·015% of iron and 0·02% of nickel).

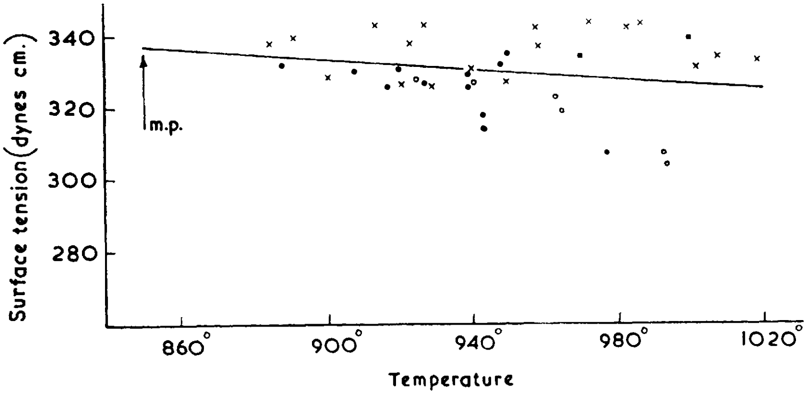

FIG. 3. Surface tension of liquid calcium.
Orifice radii: (●) 0·112, (○) 0·163, (×) 0·182 cm.

Surface tensions. These are recorded in Fig. 3. The main feature is the increasing scatter in the results at higher temperatures; this is attributed to the various complicating factors referred to above, and change in orifice radius has no obvious effect. Using the method of least squares allows us to express the results by the equation

$$\gamma = 395 - 0{\cdot}068t \quad (t = {}^{\circ}\text{c})$$

which is shown as a full line in Fig. 3 and from which the surface tension of liquid calcium at the melting point (850°) is 337 dynes/cm. From the general pattern of the results in Fig. 3 we are confident that this is the true value. The temperature coefficient, however, should at present be treated with some reserve, first, because of the larger scatter at higher temperature and, secondly, because this coefficient incorporates the temperature coefficient of density which was determined by Culpin[10] over a narrow temperature range on calcium having a melting point of 812°. The reason for the low melting points for calcium reported in earlier papers[11,12] is not known; extrapolation of the calcium–nitrogen phase diagram gives 851° as the melting point of pure calcium,[11] but it may be relevant that the presence of calcium nitride lowers this melting point.

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[10] Culpin, *Proc. Phys. Soc.*, 1957, **70**, 1069, 1079.

[11] Antropoff and Falk, *Z. anorg. Chem.*, 1934, **218**, 190.

[12] Hume-Rothery, *J. Inst. Metals*, 1926, **35**, 330.