762. *Liquid Metals. Part VII.*[1] *The Density of Liquid Barium.*

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The density of liquid barium has been measured over the temperature range 740—930°, and is expressed by the equation $\rho = 3{\cdot}476 - (2{\cdot}14 \times 10^{-4})t$, where t is in degrees Centigrade. For liquid barium, measurements are difficult because of the high chemical reactivity and the high temperatures involved. The buoyancy (Archimedes) method has been used, with a steel containing vessel and plummet. The purification of the argon blanket gas, and the attack and penetration of containing vessels by liquid barium, are discussed.

Some surface properties of solutions of barium and calcium in liquid sodium have been described in Parts V [2] and VI,[1] and volumes of mixing for these systems will also be reported in a later paper. These studies require a knowledge of the densities of pure liquid barium and calcium. The density of liquid calcium is known;[3] that of liquid barium has not previously been determined and there is even an appreciable variation in published values for the density of solid barium, as shown in Table 1. These variations are probably to be attributed to variation in the purity of the metal used. This is reflected in the melting point also; the more recent determinations give the melting point as 658°,[11] 704°,[12] 710°,[6] 714°,[13] 725°,[14] and 729°.[15]

Table 1.

The density of solid barium at 20°.

Method	Density (g./cm.^{3}) and reference
X-Ray	3·58[4], 3·61[5]
Pyknometer	3·74[6], 3·61[7], 3·54[7], 3·78[8], 3·66[9], 3·52[5], 3·50[10]

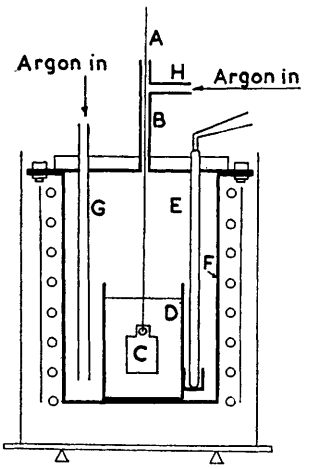
Measurements on liquid barium present particular experimental difficulties because of its high chemical reactivity and the high temperatures involved. Liquid barium attacks most of the available container materials. Culpin [3] was able to measure the density of liquid calcium at 900° by using a graphite density-bottle, but liquid barium attacks graphite vigorously. It was therefore necessary that in the method selected it should be possible to detect, and to allow for, any attack on container materials. The

[1] Part VI, Addison, Coldrey, and Halstead, preceding paper.
[2] Addison, Iberson, and Manning, *J.*, 1962, 2699.
[3] Culpin, *Proc. Phys. Soc.*, 1957, **70**, 1079.
[4] King and Clark, *J. Amer. Chem. Soc.*, 1929, **51**, 1709.
[5] Ebert and Hartmann, *Z. anorg. Chem.*, 1929, **179**, 418.
[6] Rinck, *Compt. rend.*, 1931, **193**, 1330.
[7] Weibke, Sapper, and Biltz, *Z. anorg. Chem.*, 1931, **198**, 188.
[8] Guntz, *Compt. rend.*, 1905, **141**, 1241.
[9] Richards, Hall, and Mair, *J. Amer. Chem. Soc.*, 1928, **50**, 3309.
[10] Biltz and Huttig, *Z. anorg. Chem.*, 1920, **114**, 247.
[11] Hartmann and May, *Z. anorg. Chem.*, 1929, **185**, 167.
[12] Hoffmann and Schulze, *Z. Metallk.*, 1937, **27**, 155.
[13] Schottmiller, King, and Kanda, *J. Phys. Chem.*, 1958, **62**, 1446.
[14] Keller, *Diss. Abs.*, 1959, **19**, 1915.
[15] Peterson and Hinkebein, *J. Phys. Chem.*, 1959, **63**, 1360.

buoyancy (Archimedes) method was found to be most convenient for liquid barium; the difficulties encountered in the operation of this essentially simple technique arose from an almost complete lack of knowledge of the chemical reactivity, and in particular the solvent properties, of liquid barium.

Experimental

The apparatus is shown in the Figure. The suspension wire A was attached to one arm of a balance mounted rigidly on a wall frame. The wire passed into the furnace through the copper tube B (0·4 cm. I.D.). During a measurement, the suspension wire was attached to a cylindrical steel plummet C (diam. 1 cm., length 2 cm.) of accurately known volume. The plummet was immersed in liquid barium contained in a steel beaker D (diam. 4 cm., height 7 cm.). A small cup welded to the outside of D near its base supported the platinum resistance thermometer E. The stainless-steel furnace F (diam. 8 cm., height 23 cm.) carried a bolted lid, and was wound with resistance wire in fireclay. The lid was covered with a layer of soft asbestos insulation, and the whole was contained in an outer vessel with asbestos wool



Apparatus for determination of density of liquid barium.

lagging. The resistance thermometer E was wound on a silica former, and enclosed in a steel sheath; it was connected to a controller by which the temperature could be kept constant within $\pm 2°$.

Procedure.—About 200 g. of cleaned barium were placed in beaker D under an atmosphere of pure argon, and the wire A (with plummet attached) was threaded through tube B. The furnace lid was bolted down, and at no time was the barium in contact with air. Argon flowed into the furnace through tubes G and H, and out through the top of tube B. A flow-rate of 1 l./min. was maintained throughout an experiment. The furnace was then heated to the required temperature, and the plummet weighed in liquid barium, care being taken to ensure that the plummet was not near the beaker walls or the liquid surface.

The volume of the plummet at 20°, $V_{20} = (m_{air} - m_{H_2O})/(\rho_{air} - \rho_{H_2O})$, was obtained by weighing it at this temperature in water and in air of known pressure. The volume V_t at the temperature of the experiment was then calculated from $V_t = V_{20}\ [1 + 3\alpha(t - 20)]$, with allowance for the fact that the coefficient of linear expansion of mild steel varies with temperature.[16] The density of barium (ρ_{Ba}) was then available from the relation $\rho_{Ba}V_t = (m_{air} - m_{Ba}) + \rho_{air}V_t$.

Purity of Barium and Argon.—The barium used was 99·99% pure and was cleaned by the method described in Part VI.[1] Its melting point was near 720°. At the start of an experiment the plummet rested on pieces of solid barium; on slow heating, the plummet first moved at 720°, and thereafter it could be moved freely on the end of a taut suspension wire.

Purification of the argon by passage through Linde molecular sieve (Part V [2]) is suitable

[16] "Physical Contents of Some Commercial Steels at Elevated Temperatures." British Iron and Steel Research Association, Butterworths Scientific Publns., 1953, pp. 6, 26.

for work with liquid sodium, since sodium does not appear to react with the traces of impurity in the absence of moisture. This treatment is inadequate for work with liquid barium, which reacts with traces of oxygen and nitrogen even when the argon is very dry. The argon used (British Oxygen Company Ltd.) was 99·95% pure, the main impurities being oxygen (0·0008%), carbon dioxide (0·004%), hydrogen (0·001%), water (0·0036%), and nitrogen (0·035%). The gas was therefore purified by passage through calcium turnings at 600°, followed by a 4-ft. column of Linde molecular sieve, grade 4A.

Choice of Beaker and Plummet Materials.—Iron was the most convenient material in which to contain the barium, but there are conflicting reports on its degree of resistance to liquid barium. Guntz [8] reported that barium attacks iron, and barium which had been prepared in iron apparatus contained 0·4% of iron. In contrast, Peterson and Hinkebein,[15] studying the equilibrium $Ba + CaCl_2 \rightleftharpoons Ca + BaCl_2$, observed that barium, dissolved in molten calcium chloride, did not attack stainless-steel containers. Ageev and Zamotorin [17] detected no diffusion of liquid barium into soft steel (0·08 — 0·15% of C) at 1200°. In the study of the phase diagrams for barium–calcium,[18,19] barium–magnesium,[20] and barium–lead,[21] iron crucibles were used as containing vessels.

In our experiments, four separate runs were carried out. In runs 1, 3, and 4 (Table 3) both plummet and beaker were of mild steel. In run 2, the plummet was of electrolytically pure iron, and the beaker was made from stainless steel. In each run, it was observed that the weight of the plummet immersed in liquid barium remained constant over periods of 30 min.; it was assumed that no significant attack or penetration occurred during this period, and these were the weights used in calculating the true density values given in Table 3. During this period the behaviour of the liquid barium in the beaker was normal. In the temperature range (740—920°) used, the interior of the furnace glowed at red heat, and the liquid surface could be observed through the tube B; it appeared quite clean, and the liquid metal showed no tendency to creep up the side of the steel beaker. (Liquid calcium shows pronounced " creep " [1] which will be discussed in a later paper.)

Penetration of Liquid Barium into Iron.—Change in weight of the steel plummet did occur on long immersion in liquid barium. This is attributed to penetration of the steel by the barium, and is expressed in Table 2 in terms of the error introduced into the density measurement. $\Delta\rho$ is the difference between (*a*) the measured density and (*b*) the true density deter-

TABLE 2.

Errors in density resulting from long immersion of steel plummet.

Temp.	899°	895°	840°	842°
Period of immersion in liquid barium (hr.) ...	1·25	1·50	1·75	2·0
$\Delta\rho$ (g./cm.^{3})	0·0061	0·0107	0·0130	0·0206

mined within the first 30 min. after immersion of the plummet. When an attacked plummet was washed with water, a thin film of metal flaked away to reveal the crystalline pattern of the steel. Pure iron and mild steel appeared to be attacked to similar extents.

Penetration of barium into the mild-steel beaker was observed for longer periods. After 4 hr., barium was found to have penetrated right through the 0·125-inch thick mild-steel walls of the beaker, and a layer of barium was formed on the outer walls. Analysis of borings taken from the solidified barium which had been held as liquid for 4 hr. in a mild steel beaker showed an iron content of 0·05 wt. %.

The Suspension Wire.—Wires of tungsten and of pure iron (diam. 0·008 inch) were tested; both types parted at the liquid barium surface within 30 min. of immersion. That part of the tungsten wire which had been completely immersed appeared to be unattacked; since attack is at the surface only, it may be due to minute traces of impurity (*e.g.*, oxygen) which cannot otherwise be detected. Tungsten carries a very thin (50 Å) film of the oxide WO_3, which would be reduced by barium to a tungstate (*e.g.*, $BaWO_3$). If the initial film can be re-formed, the reduction could occur progressively through the thickness of the wire. Suspension wires of 18/8 stainless steel were found to be satisfactory and durable.

[17] Ageev and Zamotorin, *Izvest. Leningrad Politech. Inst., Otdel. Mat. Fiz. Nauk*, 1928, **31**, 183.
[18] Klemm and Mika, *Z. anorg. Chem.*, 1941, **248**, 155.
[19] Sheldon, Dissertation, Syracuse Univ., New York, 1949.
[20] Klemm and Dinckelacker, *Z. anorg. Chem.*, 1947, **255**, 2.
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Results.—Density values are given in Table 3.

TABLE 3.

The density of liquid barium.

		Density of liquid barium (g./cm.^{3})				Density of liquid barium (g./cm.^{3})	
Run no.	Temp.	(*a*) obs.	(*b*) calc. (eqn. 1)	Run no.	Temp.	(*a*) obs.	(*b*) calc. (eqn. 1)
1	740°	3·3184	3·3177	3	839°	3·2974	3·2964
	741	3·3169	3·3174		844	3·2951	3·2954
	756	3·3139	3·3143				
	773	3·3136	3·3106	4	910	3·2808	3·2813
					913	3·2800	3·2806
2	804	3·3037	3·3039		928	3·2751	3·2774
	808	3·3032	3·3031				
	823	3·3050	3·3000				

The temperature–density relation is close to a straight line. When the method of least squares is used, the equation is given by:

$$\rho_t = 3{\cdot}476 - (2{\cdot}14 \times 10^{-4})t,$$

where t is in °C. Barium is compared with the other Group II metals in Table 4.

TABLE 4.

Densities at 850°, and liquid ranges for the Group II metals.

Metal	Be [22]	Mg [23]	Ca [3]	Sr	Ba
Density of liquid metal at 850° (g./cm.^{3})	1·822 *	1·338	1·362	2·28 †	3·294
M. p.	1283°	651°	850°	774°	720°
B. p.	2970°	1103°	1240°	1150°	1140°

* Density of solid beryllium. † Estimated from a value [24] of 2·6 at 20°, by assuming the coefficient of expansion for barium and the 4% volume change on fusion which is found for magnesium.[23]

The volume change on fusion of barium cannot yet be calculated, as the density of solid barium is not known over a sufficiently wide temperature range.

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[23] Liquid Metals Handbook, 2nd Edn. NAVEXOS—p. 733, U.S. Govt. Printing Office, Washington, 1952, p. 41.
[24] "Handbook of Chemistry and Physics," 1960—61, 42nd edn., Chem. Rubber Publ. Co., p. 2132.