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DENSITIES OF MOLTEN SILVER,
COPPER AND IRON

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SYNOPSIS

THE densities and coefficients of volumetric expansion of molten silver, copper, and iron have been determined by measuring the difference in the least pressures needed to release a bubble of argon from the end of a tube in each of two positions of known difference in depth of immersion. Densities at the melting points are: Ag, 9.33 ± 0.01 ; Cu, 8.03 ± 0.03 ; Fe, 7.03 ± 0.03 . Coefficients of volumetric expansion are: Ag, 1.19×10^{-4} ; Cu, 1.02×10^{-4} ; Fe, 2.16×10^{-4} .

DETERMINATIONS of the densities of molten metals of high melting point are needed for measurements of viscosity, surface tension, and change of volume on melting, the density values given in the literature being scarce and often unreliable. BENEDICKS (*ref. 20*) has studied iron, the iron-carbon system, and various ferrous alloys. From the measurements on the Fe-Ni system the density of molten nickel may be deduced. For molten cobalt the only measurement seems to have been made by KOZAKEVITCH (*ref. 1*) from the dimensions and mass of a drop.

Our measurements of density depend on determining the least pressure needed to detach a bubble from the lower end of a tube at each of two measured depths of immersion.

EXPERIMENTAL METHOD

The electric furnace is 60 cm high and 30 cm in diameter, and is heated by means of a coil of molybdenum in three sections encased in alumina having a high content of grog. The working-tube, of impermeable alumina (3, *fig. 1*), has a diameter of 5 cm, and can be replaced without disturbing the heater. The furnace is lagged with porous bricks (1), and is water-cooled (2). Rubber O-rings are used in positions (4) and at the ends of the furnace. The heater is protected with forming gas (10 vols. N_2 + 1 vol. H_2) purified by passage over heated palladium (5) followed by drying with magnesium perchlorate (6). The furnace has thermostatic control, the heating coil being one arm of a Wheatstone bridge. The temperature in the middle of the furnace can be held to $\pm 1^\circ C$; and by adjustment of the relative currents in the three sections of the heater it is possible to ensure

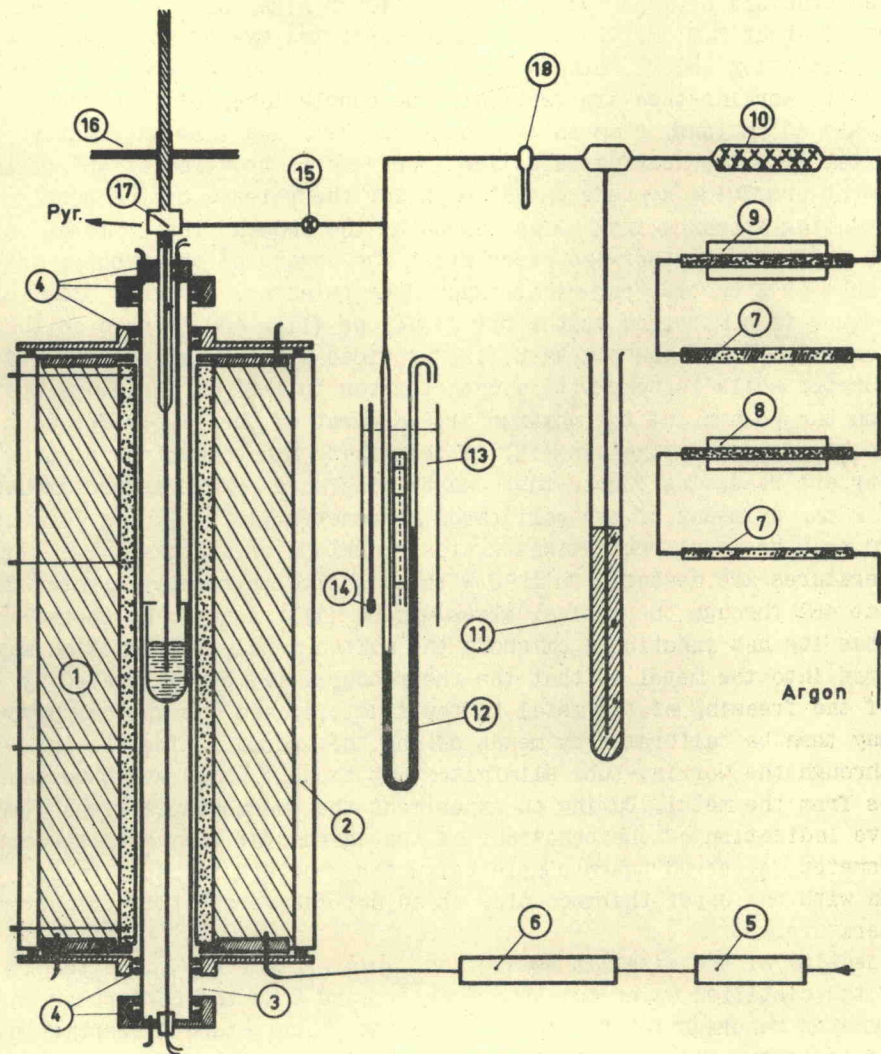


Fig. 1. General diagram of apparatus

that for 5 cm above and below the middle, the change of temperature from that in the middle is less than 2°C . The atmosphere within the working-tube is argon purified by passing through the drier (7), over finely divided iron at 200°C (8), through a second drier, over magnesium heated to 500°C in a tube of stainless steel (9), and finally through the tube (10) in which any dust is deposited. The metal occupies about two-thirds of an

untapered crucible of impermeable alumina, 10 cm high, with an internal diameter of about 3.5 cm. The crucible is supported by refractories which act as a radiation shield. Means are provided for ensuring that the furnace and its working-tube are vertical. The bubble-tube, of impermeable alumina, is 40 cm long, 6 mm in external diameter, and 4 mm internally; it is co-axial with the working-tube. The lower end is bevelled at 45°, this arrangement providing a preferential path for the release of the bubble, and preventing blockage from being caused by the sudden rise of metal in the tube which would otherwise occur after the escape of the bubble. Not more than 4 or 5 bubbles per minute should be released. For this slow rate the pressure is controlled by the oil regulator (11), and is read on the manometer (12) within the oil bath (13) provided with the thermometer (14). The manometer scale is read with a cathetometer to 1/20 mm. Readings are taken, on one column, of the maximum displacement of the liquid for each of 10 bubble releases. The tap (15) is then shut, and both limbs of the manometer are read. The bubble-tube can be displaced by a measured amount, usually 2 cm, by means of the calibrated micrometer (16) which is accurate to 1/100 mm, the usual precautions against backlash being taken.

Temperatures are measured to $\pm 3^{\circ}\text{C}$ with an optical pyrometer sighted on a mirror at 45° through the optical glass window (17). A Pt/Rh-Pt thermocouple has its hot junction 1 cm above the molten metal. The junction may be lowered into the metal so that the thermocouple may be calibrated by means of the freezing of the metal in the crucible; and the optical pyrometer may then be calibrated by means of the thermocouple. The flow of argon through the working-tube eliminates any trouble which might be caused by fumes from the metal. During an experiment the thermocouple gives a more sensitive indication of the behaviour of the thermostat than does the optical pyrometer. A second thermocouple below the crucible is used, in conjunction with the upper thermocouple, to adjust the vertical distribution of temperature.

The density of the metal is equal to $\rho_{\text{H}_2\text{O}} (h/z)$, where $\rho_{\text{H}_2\text{O}}$ is the density of the distilled water in the manometer, and h is the difference in the manometer readings for two positions of the bubble-tube differing in depth of immersion by z . As mentioned above, change in the depth of immersion is measured by means of a micrometer at the cold end of the tube. Two positive corrections must be added to the change indicated by the micrometer. The first allows for the fact that, owing to thermal expansion, the lower end of the tube moves through a greater distance than the upper end on which the measurement of displacement is made. Since both the cold and the hot ends of the bubble-tube are at almost uniform temperatures over lengths greater than that of the displacement, it follows that after enough time has elapsed for the re-establishment of the thermal equilibrium of the tube after its displacement, the hot end has moved through a distance equal

to the length, at the temperature of the hot end, of a piece of tube having a length, at the temperature of the cold end, equal to the displacement shown by the micrometer. The corrections are calculated from the data of EBERT and TINGWALDT (*ref. 25*). For a difference of temperature of 1700°C between the two ends of the tube, the correction is about 1.6%, the value depending slightly on the temperature of the colder end of the tube. The second correction takes into account the change in the height of the liquid in the crucible caused by a change in the volume of liquid displaced by the bubble-tube. Let h be the distance through which the hotter end of the bubble-tube moves, $2R$ the internal diameter of the cylindrical hot crucible, $2r$ the external diameter of the hotter end of the bubble-tube, and x the rise in level of the liquid in the crucible.

Then

$$\pi r^2(h+x) = \pi(R^2-r^2) x,$$

whence

$$x/h = r^2/(R^2-2r^2).$$

It should be noted that when the crucible and the hotter end of the bubble-tube are at the same temperature and of the same material, the value of $r^2/(R^2-2r^2)$ is independent of that temperature, and therefore it is convenient for calculation to use values of r and R which refer to room temperature. For $2R = 33$ mm, and $2r = 6$ mm, x/h is about 3½%. The correction could

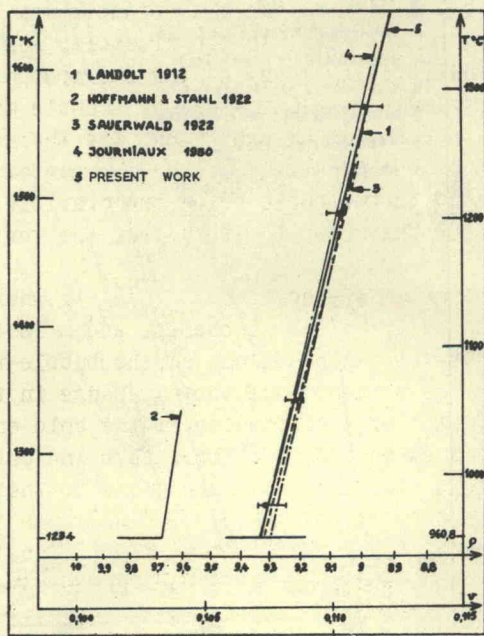


Fig. 2. Silver

be reduced by using a wider crucible, but the inner diameter of the working-tube is a limitation.

The measurements of bubble pressure, under nominally constant conditions, vary far more than would be expected in view of the accuracy of the cathetometer and scale, and these variations have a preponderant influence on the standard deviation of each set of results.

RESULTS

It was found for *silver* that the specific volume v at the absolute temperature T satisfies the equation

$$v = 0.1071 [1 + (1.19 \times 10^{-4}) (T - 1234)],$$

the melting point of silver being 1234°K.

For v , the standard deviation σ is 0.55×10^{-4} ; and for dv/dT , 0.43×10^{-8} . Our values are compared in *fig. 2* and *Table 1* with other work (*refs. 10-12*).

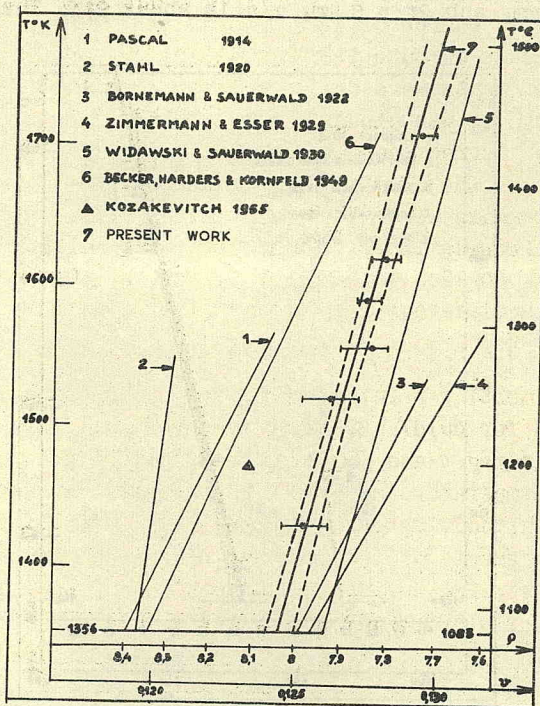


Fig. 3. Copper

Measurements on electrolytic copper are shown in *fig. 3* and *Table 2* (*refs. 13-17, 21*). Our results satisfy the equation

$$\nu = 0.1245 [1 + (1.02 \times 10^{-4})(T-1356)],$$

the melting point of copper being 1356°K. For ν , the standard deviation σ is 1.5×10^{-4} ; and for dv/dT , 1.7×10^{-6} .

Discrepancies between different workers are considerable. The experimental difficulties are discussed in *ref. 2*.

Accounts of measurements of the density of molten iron are rare. DESCH and SMITH (*ref. 18*) studied the iron-carbon system by measuring the buoyancy of an aluminium sinker, weighted by wolfram, immersed in the molten metal. No correction was made for any difference in the surface forces acting on the stem of the sinker during the calibration with mercury and the measurement on iron. ZIMMERMANN and ESSER (*ref. 17*) used the dilatometric method on metal containing 3.7% C. WIDAWSKI and SAUERWALD (*ref. 15*) used the buoyancy method for the iron-carbon system up to 4.2% C. BENEDICKS, ERICSSON, and ERICSON (*ref. 20*) determined the pressure needed to displace by a measured amount the molten metal in a macometer with magnesia tubes. The tubes were not strictly gas-tight, and reacted with the carbon in the metal. Slag formation was also a source of error. STOTT and RENDALL (*ref. 19*) made accurate measurements on pure iron by filling in vacuo a pycnometer of alumina. The experiments were delicate because of the thermal gradients in the pycnometer when it was plunged into the liquid metal heated by induced electric currents. Corrections were made for impurities in the iron, and for the expansion of the alumina, the latter correction amounting to 4%.

Our own measurements were made on purified "Orkla" electrolytic iron containing the following impurities in parts per million: C, 50; P, 1; S, 30; Si, 30; Ni, 50; Co, 100; Mn, 1; O, 200; N, 10. The numerous results, associated with 12 different temperatures, agree with the following formula:

$$\nu = 0.1421 [1 + 2.16 \times 10^{-4} (T-1809)],$$

1809°K being the melting point of iron. For ν , the standard deviation σ is 1.245×10^{-4} ; and for dv/dT , 3.8×10^{-6} . Our results are compared with those of others in *fig. 4* and *Table 3*. The table refers, not to the melting point, but to a temperature of 1550°C, for several authors have worked at this temperature without determining the thermal coefficient. Values obtained by measurements of the mass and dimensions of a drop of liquid are also included. Thus, BECKER, HARDERS, and KORNFELD (*ref. 21*) found 7.16 for the mean density of 8 drops of carbonyl iron in argon at 1510°C; 7.06, from 8 drops at 1600°C; and 6.96, from 4 drops at 1700°C. The value of the coefficient of volume expansion, α was 1.51×10^{-4} . KOZAKEVITCH and his collaborators (*ref. 22*) found 7.09 from 8 drops at 1500°C, but the spread was from 7 to 7.25.

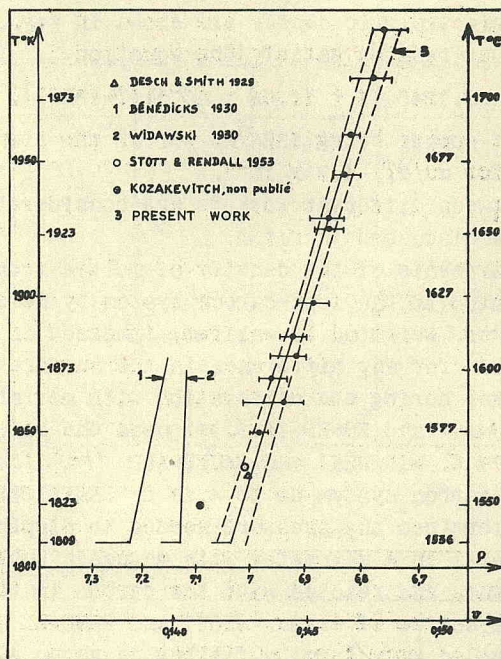


Fig. 4. Iron

Our value for the density at the melting point agrees reasonably with values in the literature, but our value of α appears to be rather high. Whilst α for Al, Sb, Bi, Pb, Cd, Ag, Au, and Cu is about 10^{-4} , it may be noted that BENEDICKS (*ref. 20*) found about 3×10^{-4} for nickel. The value for potassium is about 3.5×10^{-4} (*refs. 23, 24*); for sodium, about 3.2×10^{-4} ; and for magnesium, about 6.9×10^{-4} , although the last value is somewhat doubtful on account of the small range of temperature (650° to 750°C).

In the following tables specific volume is denoted by v ; density by ρ ; and coefficient of volumetric expansion by α .

TABLE 1
Silver at 961°C

Authors	v	ρ	$\alpha \times 10^4$
Hoffmann, Stahl, 1922	0.1033	9.68	0.83
Sauerwald, 1922	0.1073	9.32	1.11
Journiaux, 1930	0.1072	9.33	1.08
Gebhardt, (values from Landolt-Börnstein, 1912)	0.1075	9.30	1.05
Present work	0.1071 $\pm 2 \times 10^{-4}$	9.33 ± 0.01	1.19 ± 0.05

TABLE 2
Copper at 1083°C

Authors	ν	ρ	$\alpha \times 10^4$	Method
Pascal, 1914	0.1191	8.41	2	Buoyancy
Stahl, 1920	0.1196	8.36	0.55	Filling vessel
Bornemann and Sauerwald, 1922	0.1252	7.99	1.99	Buoyancy (indirect)
Zimmermann and Esser, 1929	0.1258	7.96	2.27	Dilatometer
Widawski and Sauerwald, 1930	0.1262	7.93	1	Buoyancy (direct)
Becker, Harders and Kornfeld, 1949	0.1199	8.34	1.64	Measurements on a drop
Present work, 1958	0.1245 ± 0.0005	8.03 ± 0.04	1.03 ± 0.14	Bubble pressure

TABLE 3
Iron at 1550°C

Authors	%C	ν	ρ	$\alpha \times 10^4$	Method
Desch and Smith, 1929	0.041	0.1428	7.002		Buoyancy
Widawski and Sauerwald, 1930	0*	0.1403	7.13	0.36	Buoyancy
Benedicks, 1930	0.03	0.1387	7.21	1.45	Manometric
Stott and Rendall, 1953	<0.004	0.1427	7.01		Pyknometer
Kozakevitch, 1955	<0.01	0.1389	7.2		Measurement on 2 drops
Kozakevitch (not published)	<0.01	0.1410	7.09		Measurement on 8 drops
Present work 1958	<0.005	0.1428 ± 0.0005	7.01 ± 0.03	2.2 ± 0.3	Bubble pressure

* Extrapolated

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