Review: Density Measurements in Liquid Metals and Liquid Binary Alloy Systems — A Survey

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A survey is given of the principal methods which have been used by various workers for the determination of the density (or specific volume) of pure metals and binary alloy systems in the liquid state. A selection of results obtained with the various methods for certain pure metals (Ag, Cu, Zn, Sn) and alloy systems (Cu-Sn, Ag-Sn, Bi-Sn, Pb-Sn, Cu-Pb, Ag-Bi, Ag-Pb and Hg-Tl) is displayed and discussed. The need for further systematic study of the density of alloy systems e.g. in the case of the Group Ib-IVb systems is stressed. A comprehensive survey of references to existing density measurements made on binary alloy systems up to the present time is given in an appendix.

1. Introduction
During the twenty-five years since the end of World War II, there has grown up a considerable interest in the structure and physical properties of liquids in general and of liquid metals and alloys in particular. This interest has been pursued from both the experimental and theoretical points of view. Measurements of the basic thermodynamic and transport properties have been made on a wide range of pure liquid metals and alloys by a number of workers whose results have enabled the beginnings of an understanding of the liquid state to be formed. Comprehensive reviews by Cusack [1] and Wilson [2] and also a paper by Mott [3] deal with these recent theoretical developments and give references to original papers by Mott, Shubin, Gubanov and Ziman and co-workers. The success of the present theoretical work may be gauged by the degree of agreement to be found between prediction and observation. It is therefore desirable that accurate and reliable data for such of the basic parameters, e.g. density, as have been measured should be available in a convenient form. The main purpose of this paper is to survey the methods available for the measurement of density (or its reciprocal: specific volume) of liquid metals and liquid binary alloys, when variation is permitted in the temperature and pressure parameters.

There is a certain amount of information available for the temperature-variation of density at atmospheric pressure both in the case of pure metals and some alloy systems over a range of compositions; however, some of this information is quite old and, in view of the difficulties inherent in the measurements, it is not surprising that agreement is not particularly good. With regard to the variation of density with pressure, information is rather more scanty. Postill, Ross and Cusack [4, 5] have made accurate measurements on the density and electrical resistivity of pure Hg up to a pressure of 1000 atm. and a temperature of 1100°C; an equation of state for Hg has been proposed and the relevant thermodynamic parameters have been derived by these workers. A recent survey covering experimental and theoretical work on liquid metals and vapours under pressure by Ross and Greenwood [6] contains a detailed analysis of recent density measurements, both in terms of methods and of results, on Hg and the alkali metals. These authors summarise information on equations of state, and discuss the critical point data, in addition to reviewing the electrical conductivity data on these substances under pressure. This would appear to be the definitive work in this field at the present time.

In a review of surface tension measurements on liquid metals, Flint [7] has pointed out the unreliability of some density measurements which, in their turn, vitiate many of the surface tension results. In this respect, a critical evaluation of the density data is clearly desirable. A further aspect of Liquid Metal Physics which requires reliable density data is the explanation of the observed electronic properties. As early as 1932, Birch [8] had observed that the resistance of pure liquid Hg increased as the density decreased. At the present time, theoretical interest is particularly concentrated on the electron transport properties, and whatever theory is set up to explain these phenomena the bulk density or an equation of state is required so that the electron density can be deduced on the basis of, say, the free, or nearly free, electron model.

The Radial Distribution Function, $\rho(r)$, is an important quantity introduced into structural studies and the recent theoretical treatments. This function may be expressed as the density per unit volume of atoms at a given distance, r, from a given reference atom. In order to calculate this radial distribution function for a particular metal or alloy, the bulk density must be known. In this respect, however, the major source of inaccuracy lies in the existing structural determinations rather than in the inadequacy of the available density data. A detailed account of the methods and procedure for obtaining the radial distribution functions of many liquids, including liquid alloy systems, by diffraction techniques has been given by Furukawa [9]. More recently, structural work by X-ray diffraction techniques has been reported for pure metals and liquid binary alloys by e.g. Waghorne, Rivlin and Williams [10] (Sn, Hg, Cu-Sn, Au-Ga and Au-In) and Wagner and Halder [11] (Ag-Sn, Hg-Tl, Al-Mg and Hg-In).

In addition to dealing with the continuous variation of physical properties with temperature and pressure over the liquid range, any theory of liquids must explain what occurs at phase changes; consequently, any data relating to the nature and magnitude of the discontinuity in density on melting will be relevant to the present study. In the case of liquid alloys, the volume change on mixing of the components will also be of interest.

It is against this general background that a survey and evaluation of the existing techniques and results of density measurements has been made in the following sections.

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2. Methods of Density Measurement
There is a variety of methods available for the measurement of the density of liquid metals; these will be reviewed under the following headings:

(i) Methods employing Archimedes' Principle,

(ii) Pyknometer methods,

(iii) Dilatometer methods,

(iv) Methods employing hydrostatic pressure,

(v) Other methods.

2.1. Methods Employing Archimedes' Principle
A direct and an indirect application will be considered. In the case of the *direct* application of Archimedes' Principle, a suitable inert sinker, usually a silica bulb weighted with mercury or a tungsten cylinder, is weighed when immersed in the liquid metal specimen. In the *indirect* application, the liquid metal specimen is contained in a crucible, which is weighed immersed in a bath containing a suitable, inert fused salt. An advantage of the indirect method is that the density of the solid metal and the discontinuity in density on fusion can be observed. Both methods involve considerable difficulties. In the direct method, a large volume of the liquid metal is required; thus a uniform temperature may not easily be achieved throughout the specimen and, consequently, convection currents may exert spurious forces on the sinker. For high accuracy, the volume of immersed suspension wire must be known; this usually involves the use of a probe to detect the depth of immersion of the sinker. Consequently, an accurate knowledge of the thermal expansion (and its variation with temperature if a wide range is being considered) for the sinker, the suspension and the probe is a pre-requisite. In the indirect method the physical properties of the inert liquid and their temperature-variation must be known. In both methods a surface tension correction must be applied with respect to the suspension wire. Ideally, a fine suspension should be used, but this is not always practicable, particularly at high temperatures where the changes in elastic properties with temperature may allow yielding to occur. It is also possible that condensation, either of evaporated metal from the specimen or of salt from the inert bath, may take place on the suspension wire.

In the direct method, the expression for the density, ρ_T, at a given temperature, T, is:

$$\rho_{\mathrm{T}} = \frac{\Delta M - s}{V + v_{\mathrm{s}}} \qquad (1)$$

where ΔM is the apparent loss of mass of the immersed sinker, and

$$s = \frac{2\pi \, a \, \gamma \cos \theta}{g}$$

is the surface tension correction for a suspension of radius a in a liquid for which the surface tension is γ and the contact angle is θ.

V = volume of sinker

v_{s} = volume of immersed suspension. The magnitude of s is of the order of 0.5 % of ΔM for typical metals and suspensions. In the indirect method, the crucible and liquid metal contained in it must be regarded as a composite specimen.

It is clear that the principal source of inaccuracy in either of these methods lies in the values used for γ and θ, both quantities being only imperfectly known and their measurement complicated by the fact that they are highly sensitive to the presence of impurities. One means of overcoming the difficulties introduced by this surface tension effect is proposed by Strauss et al [12] who connect the suspension wire to the sinker in such a way that the lower end is looped through a small hole at the top of the sinker and brought back to project upwards for a short distance above the top of the sinker to be parallel to the original suspension. They make two weighings with, respectively, one and two portions of the suspension wire cutting the surface of the melt. The difference in the two weighings is taken to be the magnitude of the surface tension effect on a single suspension. Alternatively, the effects of S and v_{s} in equation 1 could be eliminated by making successive weighings using sinkers of different masses on the same suspension wire and at the same depth in the melt.

A means of overcoming the difficulties introduced by the uncertainties in γ and θ has been proposed in an original method by Postill et al. [4]. In this experiment, the density variation with both temperature and pressure was studied for pure liquid Hg; in the range from room temperature and normal pressure up to 1000°C and 1000 atm, density changes from 13.5 to about 11 g. cm^{-3} were observed. The density cell as used in this experiment contained a totally immersed spherical sinker made from Ta-Mo alloy; in all, nine different sinkers were used to cover the density range quoted. For a sinker of known density, the pressure and temperature

of the mercury were first adjusted to make the liquid density very close to that of the sinker; a small further change in temperature would then cause the sinker to move from the bottom to the top of the cell or vice-versa. Thus a combination of values of p and T could be found for which the sinker would neither rise nor fall. The sinkers had been made to emit γ-rays, by previous irradiation with neutrons at AERE, and so their positions in the cells could be detected by a Geiger counter arrangment outside the pressure vessel. The results from this experiment have been presented in the form of a series of isochores, and an equation of state has been suggested.

Numerous workers over the past fifty years have employed the Archimedean technique for density measurements, largely on account of its being a fundamental method, and one which is relatively simple from the experimental point of view. Strauss states that the method was used on account of its accuracy; however any claim to high accuracy is only justified after modifications such as he describes have been made. Only a representative selection of the early references is quoted, e.g. Pascal [13] (1914 work on Zn and Cu); Sauerwald and co-workers [14] who, since the early 1920's, have investigated a range of metals and alloys. More recently, in addition to Strauss's work on Pb and Pb-Ni alloys, Gebhardt, Becker and Dorner [15] (1951, Ag, Al and alloys), Toye and Jones [16] (1958, Zn, Sn and alloys) and Kirshenbaum, Cahill and Grosse [17-20] (early 1960's Al_2O_3, Pb, Sn and Sb) have all used this technique. The surface tension treatment employed by Kirshenbaum et al, which involves an arbitrary assumption about the contact angle, and, in the case of Pb, obtains the value of the surface tension at the melting point by extrapolation from the 1927 data of Drath and Sauerwald [21], does not appear to be as satisfactory as that of Strauss or as the suggested double sinker technique. Flint [7] in his surface tension review also comments unfavourably on this treatment by Kirshenbaum.

2.2. Pyknometer Methods

The pyknometer provides an absolute determination of density. The method consists of filling a container to an accurately determined volume with the molten metal; this is then allowed to cool and the system is weighed. This method has been reported by Malmberg [22] using Cu-Pb alloys, Stott and Rendall [23] using Fe, and

Foley, Basak and Delorey [24] using Hg-Tl amalgams.

An important application of the pyknometer technique has also been employed by Cook [25] for precise measurements of the density of Hg at 20°C. In this experiment, a hollow cubical box was constructed from six blocks of fused silica. The internal dimensions of the box were of the order of 7.3 cm side length, giving a volume of the order of 390 cm³ and requiring a mass of about 5.3 kg of mercury to fill the box. The exact dimensions of the box were measured interferometrically to a high degree of accuracy; the box was filled with mercury under vacuum and an estimate of the error due to imperfect filling of the box due to the presence of chips and at edges and corners was made and shown to contribute uncertainties of 1×10^{-7} and 1×10^{-8} of the cube volume respectively. In the weighing, care was taken to avoid error due to absorption of water vapour on the surfaces of the silica box and to electrostatic charging. Absorption effects were compensated by using a nearly identical cube as a counterpoise, and electrostatic effects were eliminated by irradiating the weighing enclosure with β-radiation. The density of Hg as determined in this experiment is quoted as 13 545.884 kg.m⁻³ at 20°C and 1 atm pressure, the range of all measurements being quoted as 1.7 ppm.

The difficulties in the pyknometer method in general appear to be the possibility of incomplete filling of the vessel, unless as in the case of Cook's experiment extreme care is taken to allow for this, and the possibility of penetration of pores in the pyknometer walls to different extents by the liquid metal under test and the calibrating liquid. The volume is calibrated, usually at room temperature, by filling the container with Hg or some other liquid of well-known density; this supposes that the volume occupied by the specimen will be that occupied by the calibrating liquid, due allowance being made for the expansion of the pyknometer. From this point of view, it is desirable to design the shape of the vessel so as to avoid sharp corners which might possibly be partially filled to different amounts by the specimen and the calibrating liquid. In order to introduce the specimen into the pyknometer, it is usual to submerge the vessel in a bath containing a fairly large quantity of the metal under investigation. The pyknometer is usually evacuated or filled with an inert gas which is then slowly pumped out so that the pyknometer fills

under the action of atmospheric pressure. This technique prompts the question of whether the composition of an alloy specimen is uniform throughout the volume and whether it differs significantly from the composition of the residue in the bath. Two possibilities appear to be worthy of consideration. Firstly, in the case of an alloy in which one component is considerably denser than the other, segregation may occur; in the second case, if the vapour pressures of the components of an alloy system are markedly different, the pyknometer may tend to fill preferentially with the more volatile component. This effect could be significant in the case of an evacuated pyknometer, also at high temperatures where the volatility would be correspondingly large. Malmberg reports that to prevent slag or graphite from the anti-oxidant layer being carried down and entering the pyknometer, the inlet capillary was closed with a small plug of the appropriate metal (pure Cu for Cu-rich alloys and pure Pb for specimens at the Pb-rich end) which would then melt and allow filling to take place. This could give rise to the formation of a localised region of non-uniform density.

A disadvantage of this method is that it does not conveniently permit temperature variation to be studied, since a separate filling and weighing is necessary at each temperature. Also when a quartz vessel is used, as in Malmberg's case, a strong possibility exists for the pyknometer to crack as it cools.

2.3 Dilatometer Technique

In this case, the specimen together with an inert indicating medium is contained in a closed vessel which has a long capillary neck. The dilatometer is then placed in a fused salt bath or other suitable controlled temperature environment; changes in volume of the specimen are then observed by changes in the position of the meniscus formed by the indicating medium in the capillary neck. Clearly this method requires that the indicator should be completely inert with respect to the liquid metal specimen; careful degassing of the system is essential.

This technique has been employed by Matuyama [26] (1929, Pb-Bi, Pb-Cd and Cd-Bi alloys), by Kleppa and Kaplan [27] (1957, Hg-In alloys) and with a slight modification by Kleppa [28] (1960, alloys of Cd with In, Sn, Tl, Pb and Bi). In the Kleppa investigations, the particular interest was in the volume change on mixing. Kleppa and Kaplan used ethylene glycol at 60°C

as their indicating medium, and mineral oils at higher temperatures. A report by Perkins, Geoffrion and Biery [29] describes a more elaborate dilatometer for the measurement of density of low melting point Ce alloys using a Na-K alloy as indicator.

The difficulties of possible interaction between indicator and specimen, and of occluded gas have already been mentioned. An accurate knowledge of the expansion data for the container and for the indicating liquid is also required. In cases of a small temperature change, the expansion of the specimen may be very small leading only to a change in the meniscus shape. Consequently, for precision work, a knowledge of the surface tension and contact angle, and their variation with temperature, would be required for the indicator. A correction will also be necessary for the temperature gradient along the exposed portion of the capillary neck.

An advantage of the method is that measurements may be taken over a wide range of temperatures, with the specimen in both the solid and the liquid states. This method also lends itself with advantage to the measurement of the volume change on fusion as reported by Perkins *et al.*, or of the volume change on mixing, by using a tiltable U-shaped dilatometer cell as described by Kleppa [28].

2.4. Methods Employing Hydrostatic Pressure

Again, in this section, there are two methods, one direct and the other indirect, to discuss. The *direct* method consists of measuring the pressure required to maintain a column of liquid metal to a known height. This is done most simply in a U-tube, as described by Hogness [30]. It is, essentially, a simple method involving the use of a reference liquid of known density, and which is inert and insoluble in the liquid metal under investigation. The result is obtained by equating the hydrostatic pressures due to the two columns of liquid and applying the γ-θ corrections for each meniscus. The method is applicable over a range of temperatures, though for accurate work the variation of γ and θ with temperature must be known.

The *maximum bubble pressure* method provides a suitable indirect means of measuring liquid metal densities and has been used with success by a number of workers: Greenaway [31] (1947, Pb-Sb and Cd-Sb alloys), Fisher and Phillips [32] (1954, Pb-Sn and Cd-Sb alloys),

Taylor [33] (1954, Na), Lucas [34] (1964, Ag, Cu, Zn, Si, Ge, Sn, Sb, Bi, Te and Fe alloys), Kirshenbaum and Cahill [20] (1962, Sb), Coy and Mateer [35] (1965, Al) and Davies [36] (1966, Hg-Sn and Au-Sn alloys).

The method involves the measurement of the pressure required just to detach a bubble of an inert gas from a capillary tip immersed to a certain depth in the molten metal. In order to eliminate surface tension effects, both Greenaway and Kirshenbaum and Cahill used two separate tubes side by side but with their tips at different depths below the surface of the melt, the difference in the depths being about 5 cm. Other workers have found it more satisfactory to use a single capillary, the depth of immersion of which can be varied. A correction for the expansion of the capillary must be made together with an adjustment for the rise in the level of the surface of the molten metal when the capillary tip is lowered; these corrections have been discussed in detail by Lucas and Davies.

A typical maximum bubble pressure experimental set-up, which has been used by the authors for density measurements on Hg, is shown in fig. 1; this follows quite closely the set-up used by Davies [36]. The crucible is supported so that the liquid metal sample is located at the centre of the hot zone of the furnace and the temperature of the sample can be measured conveniently with a chromel-alumel thermocouple enclosed in a pocket at the side of the crucible. A single bubble tip is shown which can be displaced vertically through a Wilson seal device which closes the mouth of the crucible; for high working temperatures the Wilson seal may need to be water cooled. The displacement of the bubble tube is measured with a dial gauge in contact with the flat upper surface of the bubble tube. The gauge is firmly clamped to the framework supporting the apparatus, and it is essential to ensure that the spindle of the dial gauge remains vertical during use. In the arrangement shown, the entire system can be outgassed under vacuum.

The crucible is constructed from 35 mm o.d. fused silica tube and has an overall length of approximately 35 cm. The overall length of the bubble tube is approximately 50 cm., and the central capillary is made from 3.5 mm o.d., 2.0 mm bore precision silica tubing. With this set-up using silicone fluid of density approximately 1.0 g.cm^{-3} as the manometric liquid and the capillary tip located about 1 cm below the surface
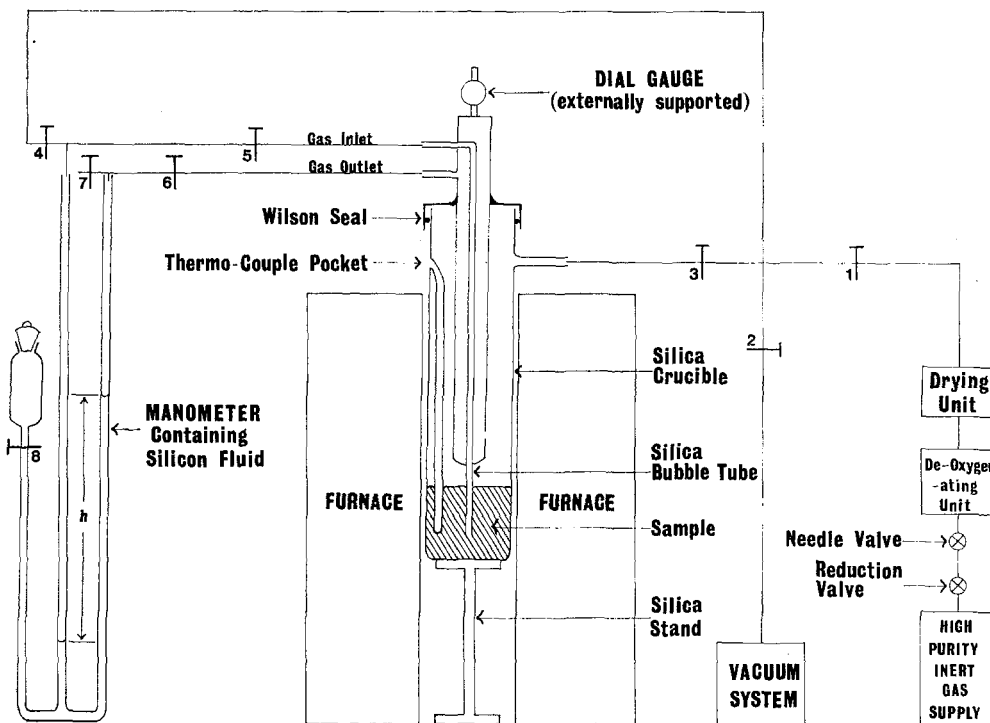
Figure 1. Experimental set-up using the maximum bubble pressure technique with a vertically displaceable bubble-tip for density measurements of pure Hg and Hg based alloys. (Based on Davis [36].)

of a mercury sample at room temperature a pressure difference, h, of the order of 20 cm of silicone fluid is obtained. A subsequent displacement of the bubble tip through 1 cm would then produce a change, Δh, of about 13 cm.

It is essential that all traces of water vapour and oxygen are removed from the bubble gas. Davies [36] has used heated zirconium chips to remove the final oxygen from high purity argon, while Lucas [34] used finely divided iron heated to 450°C also to purify argon. The choice of a gas purifying system will be governed largely by the bubble gas which is being used and also by the impurities which have to be removed.

For density measurements alone, a knowledge of the exact depth, x, of the capillary tip below the surface of the melt is not necessary, the displacement Δx can be measured accurately and more easily. The bubble pressure is usually measured with a manometer containing a liquid of density, d. Then the density of the liquid metal ρ_T is given by:

$$\rho_T = \frac{d.\Delta h}{\Delta x} \qquad (2)$$

where Δh is the difference in maximum manometer readings, before and after lowering the bubble tip. However, if a probe or some other device is incorporated so that the depth of the tip below the surface of the melt can be ascertained, then the surface tension, independent of the angle of contact, for the liquid metal may be obtained from the well known equation:

$$\frac{2\gamma}{r} = g(hd - \rho_T x) \qquad (3)$$

In this connection, it is necessary to know whether the bubble forms on the inner or outer diameter of the tip, i.e. whether the liquid "wets" the capillary tube or not. It has been suggested by some workers, e.g. White [37] that a tip chamfered at an angle of 45° might be advantageous in defining the radius on which bubbles form. A detailed study of the formation of bubbles on capillary tips has been made by Levin [38]; this work is discussed in English translation by Fesenko [39] and in the case of a non-wetting system a means is given for calculating the radius corresponding to maximum pressure. These considerations are highly relevant in the case of

surface tension measurements, but present no problem in the case of density work where it can reasonably be assumed that the bubble will form on the same radius in both positions of the capillary immersion.

Practical difficulties inherent in the method are:

(i) a reasonably large volume of the liquid metal is required but the stirring action of the bubbles should assist in the achievement of a uniform temperature throughout the specimen.

(ii) the incoming gas may be relatively cold with respect to the specimen;

(iii) the tendency of the bubbles not to break away smoothly from the tip – this can give rise to considerable "surging" in the manometer.

2.5 Other Methods

Two methods will be mentioned here, which cannot conveniently be fitted into any of the preceding categories. Firstly, a method has been described by El-Mehairy and Ward [40] which enables the density of a liquid metal, in this particular case: Cu, to be calculated from the photograph of the profile of a levitated drop. The mass of the drop was obtained from direct weighing of the frozen drop and the volume from a geometrical analysis of the photograph. Allowance was made for evaporation from the drop during the experimental run. Evaporation appears to impose a limitation on the method, in that it is only applicable at temperatures at which the rate of evaporation is not excessive. Particular advantages of the method are that it is suitable for highly reactive and refractory materials, and also surface tension considerations do not enter into the calculation of the result. A check was made on the method using a ball-bearing in place of the liquid drop. Good agreement was achieved between the values for the density calculated by this method and by more conventional methods for solids.

An elegant method for measuring the densities of a range of Pb-Sn alloys by means of γ-ray absorption has recently been reported by Döge [41]. The method is essentially simple and avoids the complications introduced into the previously described methods by thermal expansion and imperfectly known surface tension data. Döge describes measurements on Pb-Sn alloys of various compositions up to a temperature of 1200° C. γ-rays of energy 0.622 MeV from a ^{137}Cs source are used and the liquid metal specimen is contained in a tube about 2.5 cm in diameter and

between 2 and 4 cm long depending on the anticipated amount of absorption.

For a binary system, Döge quotes the formula:

$$V = \frac{N(n_a\mu_a + n_b\mu_b)\, x}{\ln(I_0/I)} \qquad (4)$$

for the calculation of the mean atomic volume, V, where the other symbols are:

N = Avogadro's number

n_a and n_b respectively the atomic fractions of components a and b.

μ_a and μ_b respectively the γ-absorption coefficients for the components a and b.

x = length of specimen traversed by γ-ray beam

I_0 = incident intensity

I = emergent intensity.

Values for μ_a and μ_b are obtained from absorption measurements on solid specimens of the pure components a and b, whose bulk densities can be obtained by conventional means. These solid specimens have the same geometrical shape as the liquid metal specimen in its container. The method appears to depend on the ability of the instrumentation to detect small changes in the emergent intensity, I. Döge claims that the error in his ratio (I_0/I) lies in the region of 0.3 to 0.7%

2.6 Discussion of Methods

In methods where the effects of surface tension and contact angle cannot be eliminated, there would appear to be little value in attempting to suggest a quantitative assessment of accuracy, since the uncertainties associated with γ and θ will be, at least, as large as the observational uncertainties. In the other methods, where the principal observations are of mass, volume, position and displacement of a meniscus, the uncertainties in observation should all be small, since these are all quantities which are measurable with a reasonably high degree of precision. The main source of inaccuracy would then appear to lie in systematic error.

The direct and indirect Archimedes' Principle techniques have much to recommend them, in that they present a fundamental approach to the problem of density measurement. The density is calculable directly in terms of the difference between two masses and a volume, and as has been pointed out these are measurements where a high degree of accuracy should be possible. However, the uncertainty introduced by the surface tension factors renders the results obtained from single-bob techniques too unreliable to be of much value. Modifications such as that suggested

by Strauss and the double-bob technique, which enable the surface tension effects to be handled in a realistic fashion, are much to be preferred to corrections which depend on rather uncertain data. The method described by Postill et al. completely eliminates the surface tension effects; this method has, as yet, only been used with pure Hg, however it would clearly be equally applicable to liquid alloys of known composition. The technique does not appear to lend itself easily to a progressive variation in solute concentration in the case of liquid alloys.

In the case of pyknometers and dilatometers the major difficulties encountered are the practical ones of incomplete filling, bubble formation and preferential evaporation of alloy components. This last consideration makes the pyknometer, in particular, rather more suitable for pure metals than for alloys. Here, the determination at only one temperature is a disadvantage. The difficulties due to expansion and surface tension data in the case of the dilatometer have been stressed. This instrument appears to be most useful for the meaurement of volume changes on fusion and on mixing; since these phenomena will occur at a definite temperature, the effects of thermal expansion and temperature dependent surface tension changes in the indicator will be largely overcome.

The principal features in favour of the maximum bubble pressure method are that it successfully eliminates the surface tension effects and their temperature variation, and also that it permits a progressive increase in solute content to be made, as has been described by Davies. Since a new clean surface is formed with each bubble, the effects of surface contamination are minimised. The method is convenient, applicable over a wide range of temperatures and has been found reliable by a large number of workers. However, Williams and Freeman, Fulmer Research Institute, (private communication, 1967) found inconsistencies in density values, when trying to measure density and surface tension simultaneously for liquid Cu and liquid Sn by plotting the observed maximum bubble pressure against known depth of immersion of the bubble tip and interpreting the graph according to equation 3. It has subsequently been reported (Fulmer Research Institute, private communication, 1970) that consistent values for surface tension and density measured simultaneously have now been achieved with specimens of liquid Cu, Sn and U using a specially prepared

thin-walled alumina capillary tip of approximately 2 mm bore. With care, it was found that wall thicknesses of about 0.1 mm and values of about 0.9 for the ratio of internal to external radii could be obtained. These factors enabled the radius on which the bubble formed to be determined quite accurately. The problem of surging, due to irregular breaking away of bubbles was overcome by the use of pure helium as the inert gas, both for the atmosphere and for bubble formation; this success is attributed to the higher thermal conductivity and the lower viscosity of helium as compared with argon,which had been used previously. In the case of surface tension measurements, the position of the liquid surface was detected without the aid of electrical probes simply by lowering the bubble tip slowly and observing when a pressure difference was first detected on the manometer. The technique of varying the depth of immersion of a single bubble tip used by Lucas, by Davies and by the workers at Fulmer is preferable to the double capillary used by Greenaway and by Kirshenbaum, since the two tips will not be truly identical and the longer tube is likely to impede the breakaway of bubbles from the higher tip.

The accuracy attainable in the maximum bubble pressure method should be good; the calculated result depends on the known density of the manometric liquid which is usually double distilled water or silicone fluid of low vapour pressure, on the measured displacement of the capillary tip and on the difference between the maximum readings observed on the manometer. The capillary displacement is usually measured at the cold end of the bubble tube using a micrometer device, consequently a correction for the expansion at the hot end will be necessary. The manometer readings will in general be taken with the aid of a cathetometer. An overall accuracy of better than $\pm \frac{1}{2}\%$ might therefore be expected.

The choice of method to be used in a given investigation will be governed to a large extent by the liquid metal or alloy system to be studied. Factors affecting this choice are, for example, the temperature range over which the specimen is liquid and in particular the upper limit of this range, the chemical activity of the metals with respect to the material of the container and also to the atmosphere above the specimen or to any indicating liquid that may be present. Particular requirements of the investigation such as the dependence of the density on pressure or the study of volume changes on melting or mixing

will also impose restrictions on the choice of methods available. Of the methods surveyed, only that of Postill *et al* is suitable for the investigation of the dependence of density on pressure; the dilatometer methods of Kleppa *et al* are particularly suitable for studying the changes in volume that occur on melting or on mixing two alloy components at a fixed temperature.

Lucas states that his choice of the maximum bubble method was decided by the particular need for accurate values of the liquid density of high melting point metals. Measurements showing the variation of density with temperature in the region just above the melting points for platinum (1769 to 1850°C) and for palladium (1552 to 1800°C) have been made [42] with this method. On the other hand, this method has been used by the same team, Übelacker and Lucas [43], at much lower temperatures for Sn, Zn and Sn-Zn alloys, also by other workers, e.g. Fisher and Phillips for Pb-Sn alloys.

With regard to chemical activity, crucibles, bubble tubes, sinkers etc. can be constructed from silica for most of the lower melting point metals except Al, and from alumina or molybdenum or tungsten in the case of the higher melting point metals and Al. High purity argon has been widely used to provide an inert atmosphere above the specimen and also as a bubble gas; Strauss *et al.* report having used a reducing argon-hydrogen mixture as a cover gas in their Archimedean study of Pb and Pb-Ni alloys. However the recent evidence reported by the workers at the Fulmer Research Institute would suggest that helium is the preferred working gas.

It is suggested that the maximum bubble pressure method is, in general, the most suitable for the measurement of liquid metal densities because the uncertainties due to surface tension effects are most convincingly removed, it is convenient and applicable over a wide range of temperatures, and it is also reasonably accurate. The modified Archimedes' techniques should
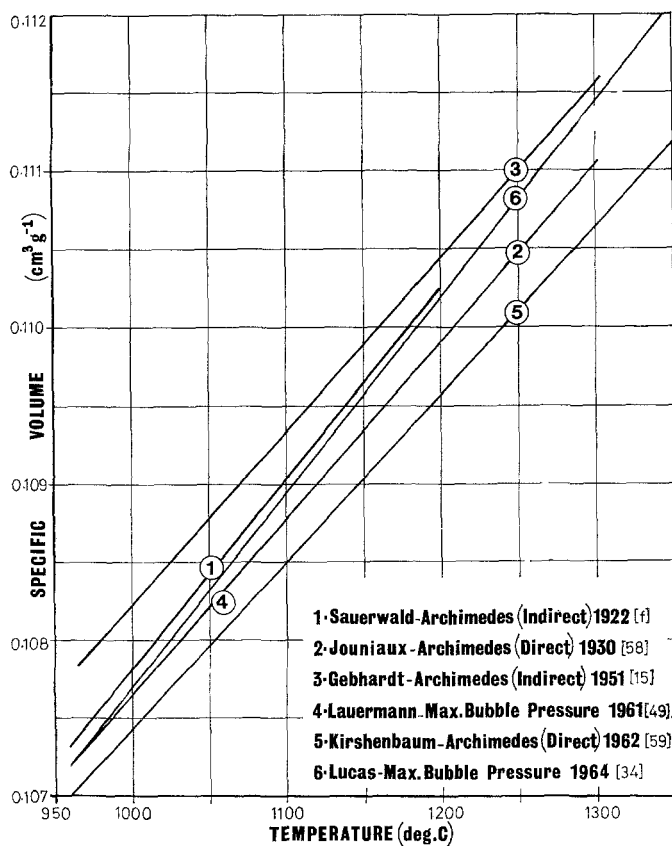

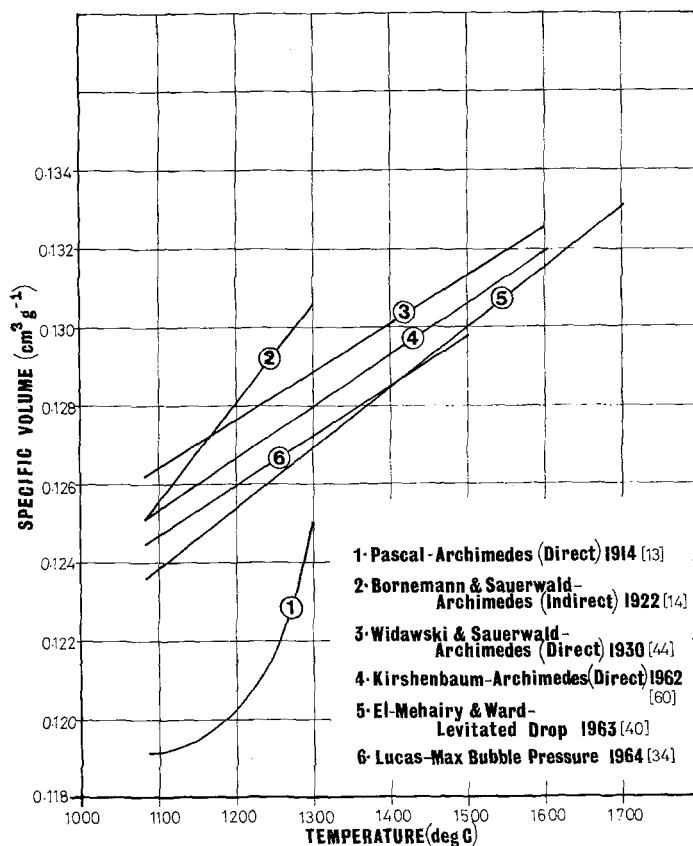*Figure 2* Variation of specific volume of pure Ag with temperature.

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Figure 3 Variation of specific volume of pure Cu with temperature.

also be reliable. It seems likely that, in the future, the γ-ray absorption method may become more widely used on account of its ease and convenience; it should also be capable of application over a wide temperature range.

3. Analysis of Results

Results for pure metals and for alloys will be discussed separately.

3.1. Results for Pure Metals

In general, reliable density values for most of the pure metals are adequately tabulated in readily available reference works. In addition, a review of results for elements in Groups I (Ag, Cu); II (Zn); IV (Si, Ge, Sn); V (Sb, Bi); VI (Te) and VIII (Fe, Co, Ni, Pd, Pt) has recently been presented by Lucas [34], in which equations relating specific volume and temperature are given and discussed. A selection of these results is displayed graphically in figs. 2 (Ag); 3 (Cu); 4 (Zn) and 5 (Sn). For Ag and Zn, it can be seen

that the agreement between the results obtained by various workers using different methods is reasonably good, of the order of 1%, both in terms of ρ_T and $d\rho_T/dT$. In the case of Cu (fig. 3), the early results of Pascal [13], are shown to be completely at variance with the more recent results of other workers. Since the work of Widawski and Sauerwald [44] using the same method as Pascal has yielded results more in accord with contemporary values, e.g. Lucas [34] and Kirshenbaum [60], it must be concluded that Pascal's work is unreliable. Also, the slope of the line representing the results of Bornemann and Sauerwald [14] does not agree well with the other data; the method used in this particular investigation was the indirect Archimedes technique, where the influence of convection currents can be highly significant. In any case, these results must now be regarded as having been superseded by the slightly more recent work of Widawski and Sauerwald.

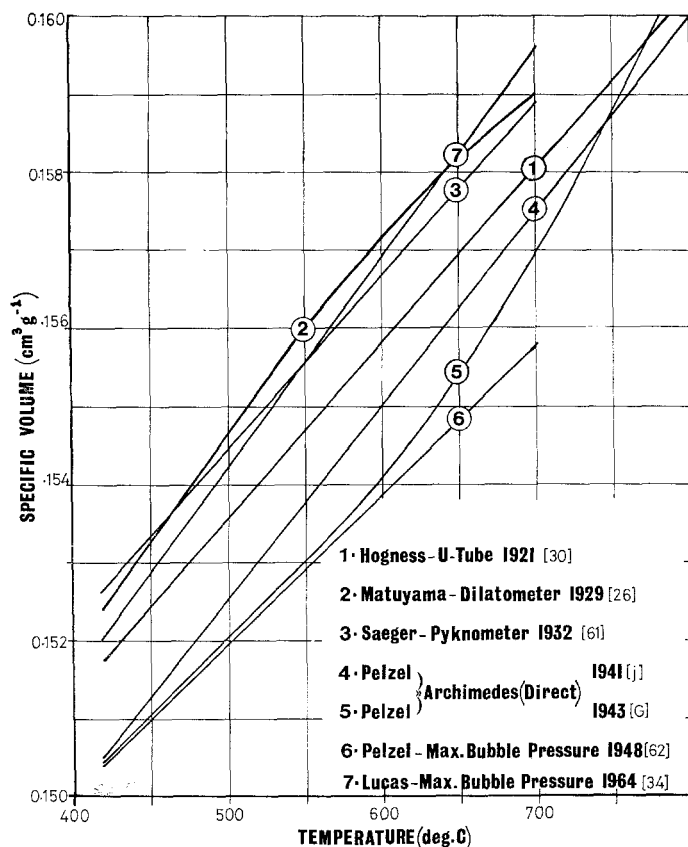The graphs for Sn (fig. 5) show remarkably

1. Hogness - U-Tube 1921 [30]

2. Matuyama - Dilatometer 1929 [26]

3. Saeger - Pyknometer 1932 [61]

4. Pelzel ⎫
            ⎬ Archimedes(Direct)   1941 [j]
5. Pelzel ⎭   1943 [G]

6. Pelzel - Max. Bubble Pressure 1948 [62]

7. Lucas - Max. Bubble Pressure 1964 [34]

Figure 4 Variation of specific volume of pure Zn with temperature.

good agreement betwen the various methods that have been employed. Lucas [34] tabulates and points out the agreement obtained in the results of some twenty workers, using all the methods that have been discussed in this paper. For the sake of simplicity only a limited selection of the results discussed by Lucas has been exhibited in fig. 5.

3.2. Results for Binary Alloys

In the case of alloys, information is less easily available than for pure metals. Sauerwald and various co-workers [45-47] have proposed a classification of binary alloy systems based on observations over a wide range of physical properties. This scheme provides a reasonably satisfactory way of studying binary alloy systems for which sufficient data is available; the systems are arranged into four main groups:

(a) *V systems (Verbindung – Compound)* This group contains those systems in which fairly strong intermetallic linkages known to be present

in the solid phase show evidence of existing in the liquid.

(b) *L systems (Lösung – Solution)* These systems show no anomalies and in the purest form are ideal solutions.

(c) *E systems (Entmischung – Segregation)* This group contains those systems which show tendencies towards segregation, i.e. those which exhibit miscibility gaps in the liquid phase.

(d) *Z systems (others)* In certain cases where no highly characteristic features are exhibited or where the available data may be unreliable or inadequate, the placing of a particular system into one of the foregoing categories would not be satisfactory. Such systems are brought together into this fourth group.

Table I shows the Sauerwald classification for a number of the more widely studied binary alloy systems.

In a recent review of the physical properties of liquid alloy systems between the Group Ib and IVb elements, Mott [48] has pointed out that a
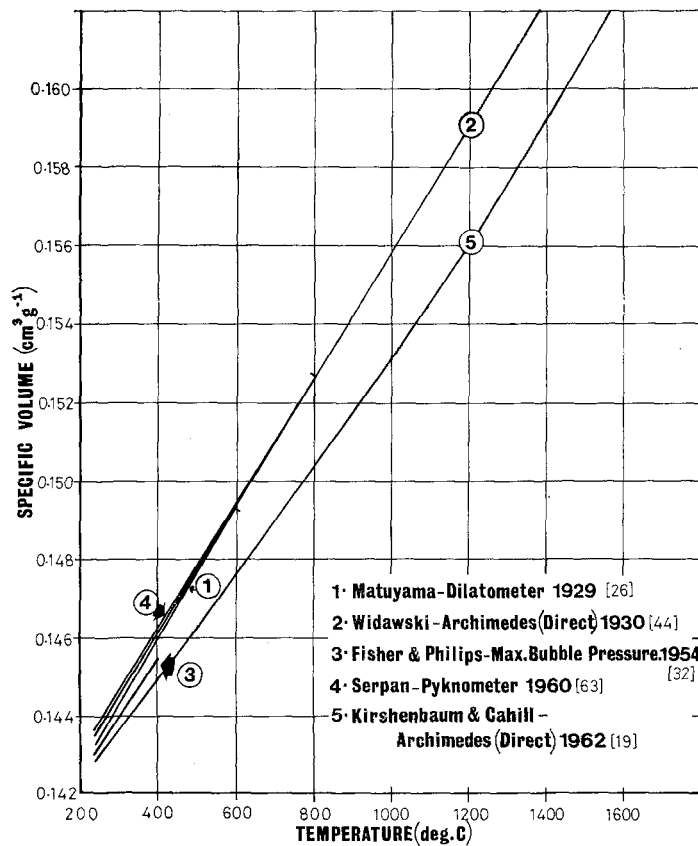
455

Figure 5 Variation of specific volume of pure Sn with temperature.

strong tendency exists for these systems to exhibit a maximum departure from ideal solution behaviour at a composition of approximately 75 at. % of the noble metal. The evidence available suggests that in conditions which favour the formation of stable compounds in the solid state, anomalies are frequently observed in physical properties in the liquid state, particularly in the region close to the melting point. It is postulated that at these compositions the formation of a resonating covalent type of liquid metal bond is most strongly favoured. The behaviour of Pb with the noble metals is such as not to show up this postulated effect as clearly as that of Si, Ge and Sn. These observations are consistent with V systems in the Sauerwald classification. Unfortunately, the reported density data on Group Ib-IVb systems is by no means comprehensive.

A representative selection of results for various alloy systems across the Sauerwald classification is displayed in figs. 6 to 13 inclusive (V systems: Cu-Sn and Ag-Sn; L systems: Bi-Sn and Pb-Sn;

E systems: Cu-Pb, Ag-Bi and Ag-Pb; and Z systems: Hg-Tl). It must be stressed that the information displayed in these figures may not necessarily cover the full range of temperatures studied in the work quoted. The aim, in this paper, is to show the general tendency of variation of specific volume with composition and temperature. For completeness, the original reference should be consulted.

3.2.1. V Systems

For Cu-Sn (fig. 6), the results of Bornemann and Sauerwald [14] are displayed for various temperatures, and similarly for Ag-Sn (fig. 7) the results of Lauermann and Metzger [49] are shown. Both sets of curves show a change of slope, strongly marked in the case of Cu-Sn and rather less strongly so in the case of Ag-Sn, in the region of 75 at. % of the Group Ib metal, which is consistent with Mott's observation. This change of slope is not, however, shown by the much earlier data (1912) for Ag-Sn taken from

TABLE I The Sauerwald Classification for some of the more common binary alloy systems. (See refs [45-47])

V Systems (Intermetallic)	L Systems (Solution)	E Systems (Segregation)	Z Systems (Others)
Ag-Sn*	Ag-Si*	Ag-Bi	Al-Mg
Al-Cu	Al-Zn	Ag-Pb*	Bi-Pb
Al-Ni	Bi-Cd	Al-Sn	Cd-Hg
Al-Sb	Bi-Hg	Cu-Fe	Co-Fe
As-Cd	Bi-Sb	Cu-Pb*	Cr-Fe
Au-Sn*	Bi-Sn	Ga-In	Cs-Na
Be-Ni	Cd-In	In-Zn	Fe-Ni
Bi-K	Cd-Pb		Hg-In
Bi-In	Cd-Sn		Pb-Tl
Bi-Tl	Cd-Tl		Sb-Sn
Cd-Mg	Cd-Zn		
Cd-Sb	Co-Cu		
Co-Si	Cs-K		
Cu-Sn*	Cs-Rb		
Fe-P	Cu-Ni		
Fe-Pd	Fe-Mn		
Fe-Si	Ga-Zn		
Ga-Sb	Hg-Pb		
Hg-K	Hg-Tl		
In-Sb	Hg-Zn		
Mg-Ni	In-Pb		
Mg-Pb	In-Sn		
Mg-Si	K-Na		
Mg-Sn	K-Rb		
Mg-Tl	Na-Rb		
Mg-Zn	Pb-Sb		
Mn-Ni	Pb-Sn		
Mn-Si	Sn-Tl		
Ni-Si	Sn-Zn		
Sb-Tl			

Alloy systems of the groups Ib-IVb are marked*.

the Landolt-Börnstein Physikalisch-Chemische Tabellen and quoted by Gebhardt, Becker and Tragner [50] in a report of a viscosity investigation. The reliability of these early density values is very much open to question; this emphasises the need once again for up-to-date, reliable data. The work of Lauermann and Metzger on Ag-Sn is regarded as being reliable.

No subsequent study of the density of the Cu-Sn system appears to have been made since that of Bornemann and Sauerwald; thus, although the data are now nearly fifty years old, they remain, by default, the best available.

3.2.2. L Systems
For Bi-Sn (fig. 8) the results of Bornemann and Siebe [51] are shown for temperatures of 300° and 700°C. These curves show certain fluctuations for which no entirely satisfactory explanation can be offered other than that the authors state that some extrapolated values are used. These fluctuations are definitely reproduced in the original published graphs of Bornemann and Siebe. This system has been studied recently by Predel and Emam using a pyknometer method [52]; the results of these workers show an almost linear relationship between density and concentration (vol. %) from pure Bi to pure Sn at 300°C. The results of Predel and Emam,
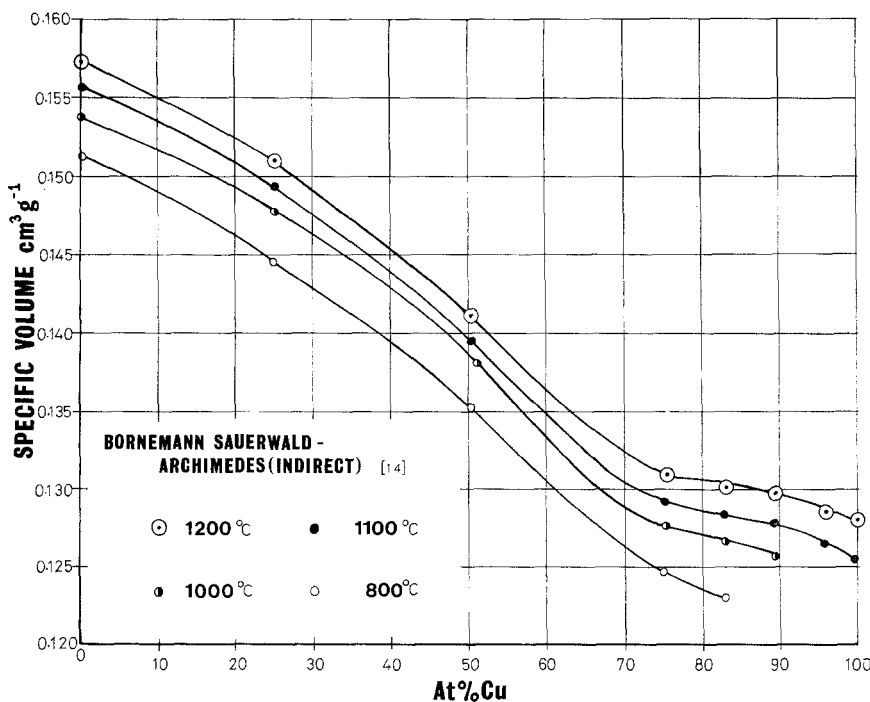

Figure 6 Variation of specific volume with composition for the alloy system Cu-Sn.
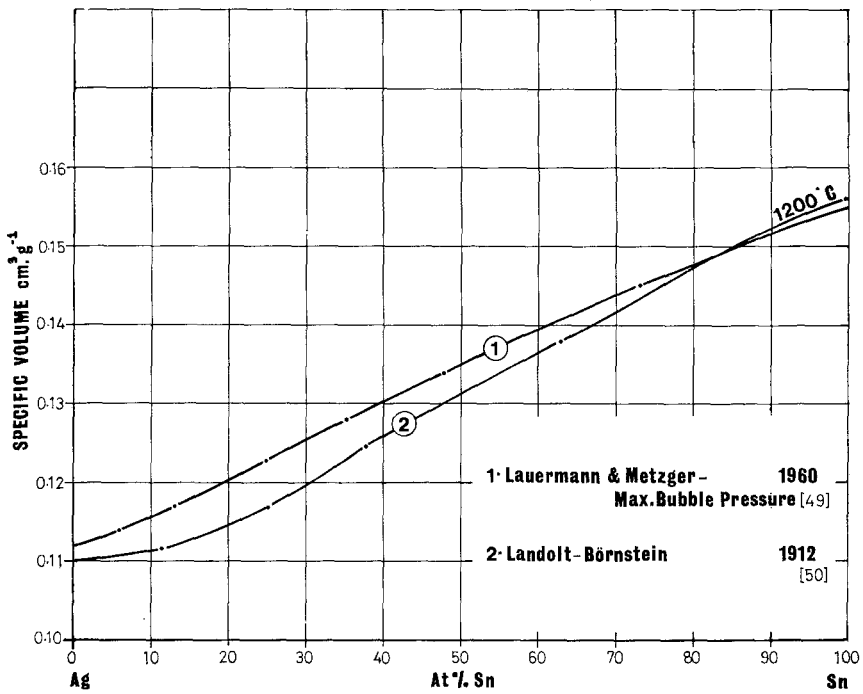
Figure 7 Variation of specific volume with composition for the alloy system Ag-Sn.
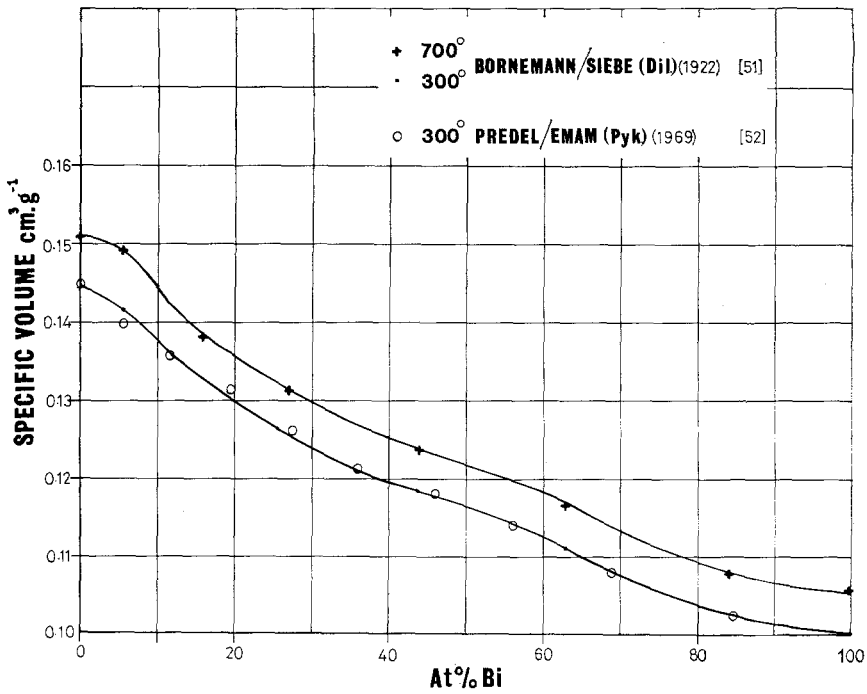

Figure 8 Variation of specific volume with composition for the alloy system Bi-Sn.
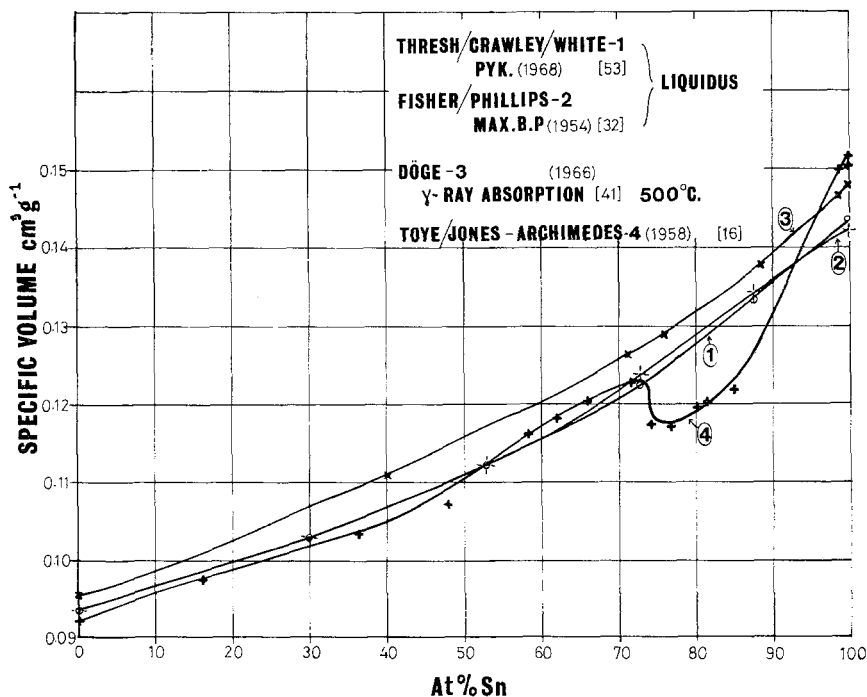
Figure 9 Variation of specific volume with composition for the alloy system Pb-Sn.

converted to concentrations in at. %, are also displayed in fig. 8 and then appear to confirm the earlier work.

In the case of Pb-Sn (fig. 9), good agreement is shown between the results of Fisher and Phillips [32] and those of Thresh, Crawley and White (1968, pyknometer method) [53] along the liquidus at low Sn concentration; above 65 at. % Sn a slight departure is noticed between the two sets of results. The results of Toye and Jones [16] are also shown for the liquidus, but these results indicate a marked anomaly above 70 at. % Sn which, since it is not found by any other workers with this system and has no theoretical explanation offered by Toye and Jones, is regarded as spurious. Thresh *et al.* suggest that this anomaly is experimental in origin. The values obtained by Döge [41] at 500°C yield a curve which is essentially parallel to that obtained along the liquidus by Fisher and Phillips and Thresh *et al.* Döge's work is regarded as reliable in view of the general agreement obtained and the elegance and essential simplicity of the method employed.

3.2.3. E Systems

For the system Cu-Pb (fig. 10) the results of Pelzel (1957, Archimedes' method) [54] do not appear to be in agreement with those of Lucas [34] and other workers for pure Cu – Pelzel's values for the specific volume being considerably higher than those shown in fig. 3 at corresponding temperatures. In addition, Pelzel does not state whether he is considering concentrations in weight or atomic percentages; in the absence of definite information on this point, it has been assumed for the purpose of this work that Pelzel's values were originally quoted in wt. % and they have accordingly been converted to at. % for display in fig. 10. Malmberg's [22] values for Cu-Pb at 1110°C are also shown expressed in at. %; these results are in reasonably good agreement with the values of Lucas and other workers for pure Cu at 1100°C. However, if Pelzel's values for composition were taken as being originally expressed in at. % then the curves would show a better fit with those of Malmberg, but the anomalous values at the pure Cu end would still remain. Pelzel's results as quoted in his paper also show an anomalous value for the specific volume of pure Pb at 1100°C; it is thought that this could well be a misprint in the original publication. In the absence of other confirmatory data for this system, Malmberg's results must be considered
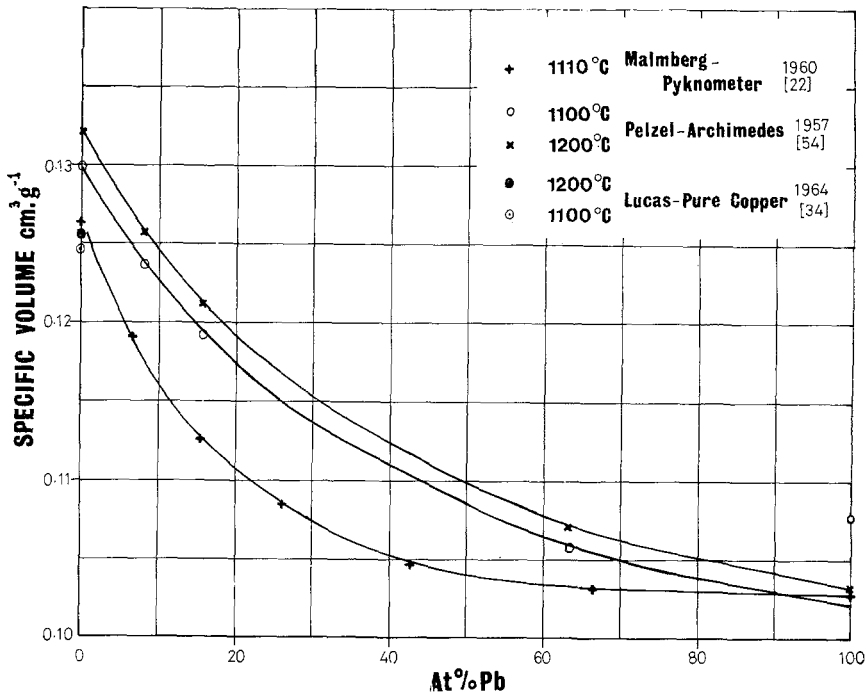
459

Figure 10 Variation of specific volume with composition for the alloy system Cu-Pb.

as being superior to those of Pelzel; this system should, however, be more thoroughly investigated.

The curves for Ag-Bi (fig. 11) and for Ag-Pb (fig. 12) are based on the data quoted by Sauerwald, Kepp and Metzger (1966, maximum bubble pressure method) [55]. In the original publication, the data is displayed by plotting specific volume against concentration in wt. % of the base metal at various temperatures, and in the case of Ag-Bi, a relatively straight portion of the curve is obtained at all temperatures for the higher Bi concentrations. It can be seen, despite the small scale of the figure in the original report, that not all the experimental points fit the curve exactly as drawn; the authors offer no explanation as to why these points off the curve are less heavily weighted than the others. However, if, as in this case, the data are displayed as specific volume against at. % Bi, a set of points is obtained through which a smooth curve can be drawn showing a continuous change of slope. In fig. 12, the curve for Ag-Pb at 1000°C shows a very marked change of slope in the region of 60 at. % Ag.

Clearly these systems, for which no other data appear to be available, should be further investigated.

3.2.4. Z Systems

The system Hg-Tl (fig. 13) is liquid at room temperature up to a concentration of about 45 at. % Tl. The results of the early work (1919) by Richards and Daniels [56] using a pyknometer method are in good agreement with the more recent work by Abowitz and Gordon (1963, dilatometer method) [57]. At 30°C the specific volume varies almost linearly with composition over the range in which the system is liquid. No reported density data for Hg-Tl at temperatures above room temperature and for concentrations above 40 at. % Tl has been found, except for the recent work of Predel and Emam [52] who report values up to 200°C and 40 at. % Tl. These authors point out that in the case of Tl rich alloys the liquidus temperatures are not very far below the normal boiling point of pure Hg and at these concentrations a significant loss by evaporation occurs, consequently they restricted their investigation to the ranges quoted. Within this limitation, an almost linear plot of density against composition up to about 40 at. % Tl was obtained at 200°C. The published data now available for the Hg-Tl system would justify its inclusion in the L group of the Sauerwald classification.
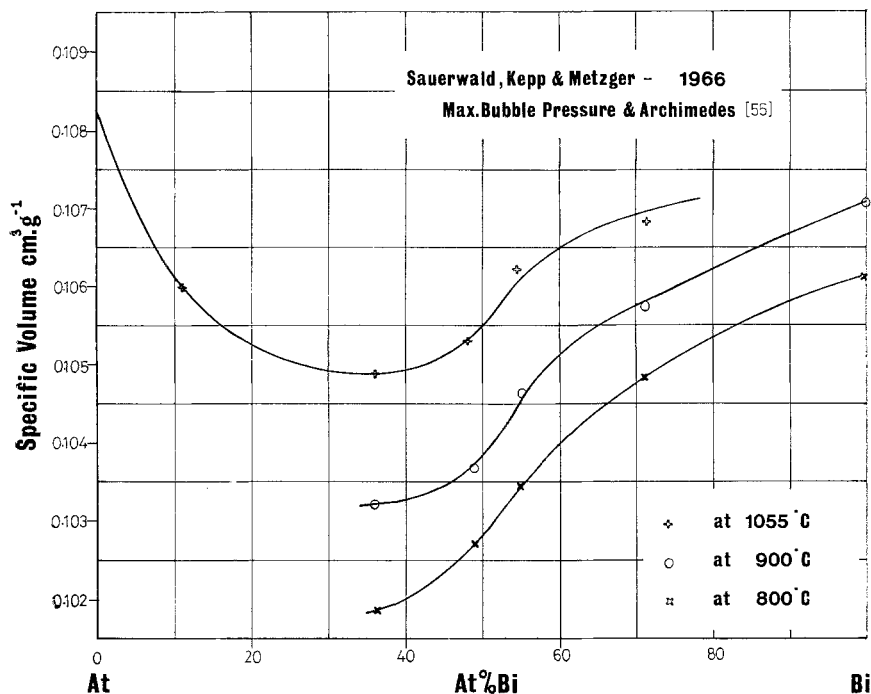
460

Figure 11 Variation of specific volume with composition for the alloy system Ag-Bi.

Predel and Emam also report density measurements on a number of systems including the Z systems: Hg-In, and Pb-Tl. For Hg-In at 200°C, the density decreases almost linearly with composition up to about 70 vol. % In but above this concentration the decrease is rather more rapid. In the case of Pb-Tl at 500°C, the density versus concentration (vol. % Tl) curve is not linear; the density increases only slowly up to about 75 vol. % Tl, but after this point the increase is more pronounced.

4. Conclusions

The survey of methods for the measurement of the densities of liquid metals suggests:

(i) that the methods based on the direct or indirect applications of Archimedes' Principle are essentially simple to carry out and are capable of yielding high accuracy provided that the effect of surface tension forces acting on the suspension is taken into account. The significance of this proviso was probably not fully grasped by the pioneer workers with this method and their results must accordingly be weighted rather less heavily than more recent work.

(ii) that pyknometers are particularly suitable for density determinations at a particular tempera-

ture. In fact, the present standard value for the density of pure Hg at 20°C was obtained by a pyknometer method and an accuracy of the order of 1 part in 10^6 is claimed.

(iii) that the dilatometer is best suited to the measurement of volume changes on mixing and on fusion etc. Again, results obtained by the early workers with this method, e.g. Matuyama, are not now regarded as highly reliable. The technique has been considerably refined by Kleppa *et al*, whose results can be taken with confidence.

(iv) that the maximum bubble pressure method is probably the most convenient and reliable method available at present and is capable of yielding a reasonable degree of accuracy. It has been used with success on both pure metals and alloys by a considerable number of workers. The use of helium as both a cover and a bubble gas by the Fulmer workers seems to have removed the doubts about the suitability of this method for the simultaneous measurement of density and of surface tension.

Density data are available for most pure metals over the ranges of temperature in which they are liquid. However, in the case of binary alloy systems the availability and reliability of
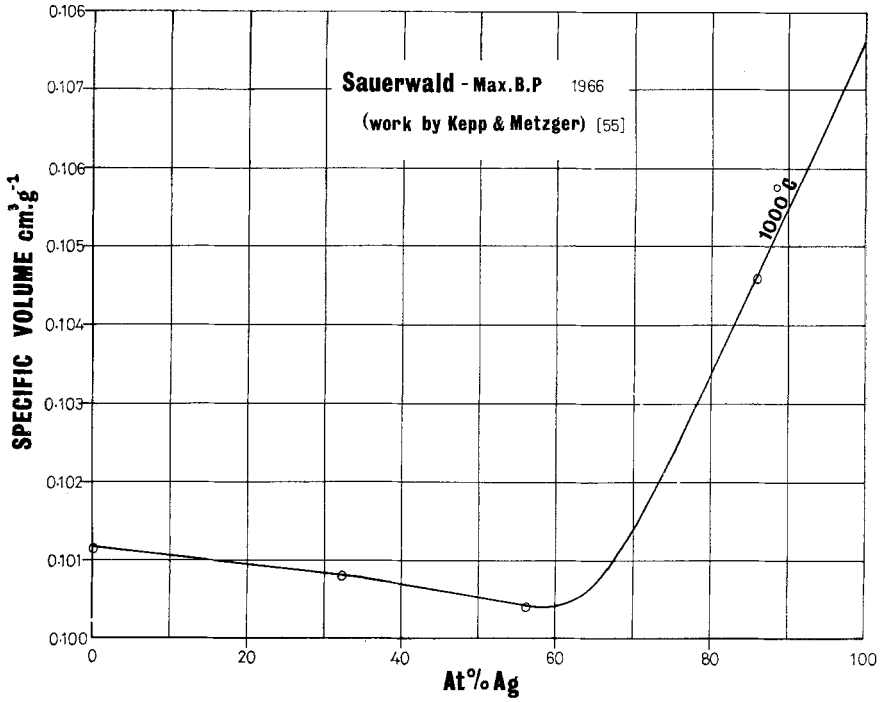
461

Figure 12 Variation of specific volume with composition for the alloy system Ag-Pb.
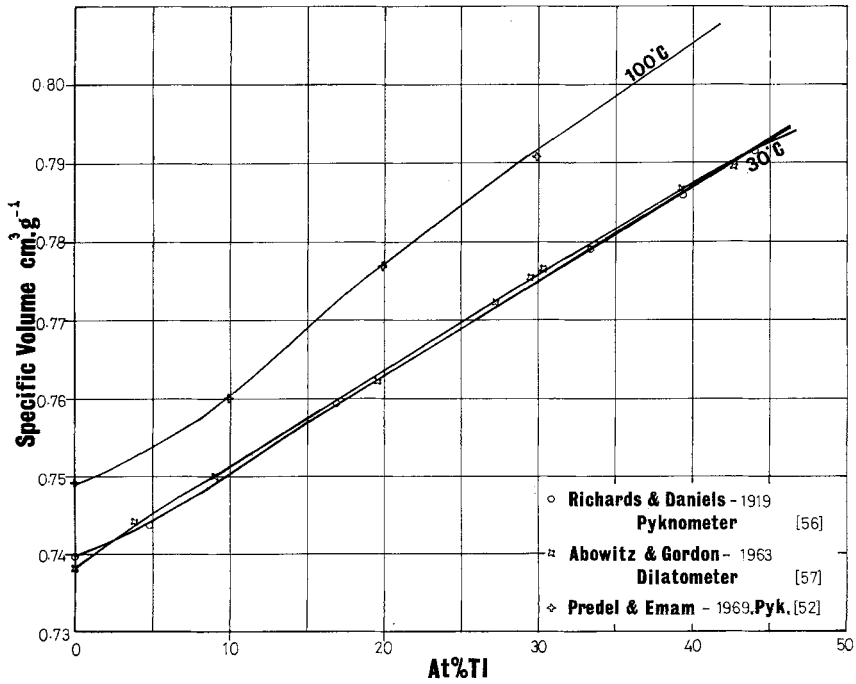

Figure 13 Variation of specific volume with composition for the alloy system Hg-Tl.

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the density data is a much more haphazard affair. A wide range of alloy systems, especially those which are liquid at relatively low temperatures: say below 1000°C, appears to have been studied in terms of a variety of physical properties and in many cases it would seem that density measuremens have been made rather as a secondary consideration as and when these values have been required. Little confirmatory evidence appears to exist for many systems whose densities have been measured in these circumstances. Without any wish to belittle the efforts of the pioneer workers in the field of density measurements, it must be stated that a significant amount of the data on binary alloys which are available for reference at the present time is old and not highly reliable. In cases where the same system has been studied by different workers the agreement that has been obtained has not been in every particular case, e.g. Cu-Pb, noticeably good.

Of the systems referred to in this paper, it is evident that the systems Bi-Sn and Cu-Pb could well be restudied to investigate the fluctuations and anomalies previously mentioned. It would be desirable that the densities of Hg amalgams be systematically studied, but the relatively low boiling point of pure Hg imposes major difficulties here as reported in the case of Hg-Tl by Predel and Emam. Considerable scope exists for a systematic study of densities of the alloy systems of the Group Ib-IVb metals.

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Appendix

Existing results of density measurements on liquid, non-ferrous binary alloy systems are summarised in table II. A previous table has been published by Faber and Ziman [A1] giving references for both electrical resistivity and density measurements up to the early 1960's. In this summary we attempt to make the survey of density measurements comprehensive up to 1970. The same principle set by Faber and Ziman has been followed here, i.e. a set of measurements for an alloy system XY, say, which spanned the whole range of concentrations is entered twice under both X and Y as solvent; but a set of measurements which covered only one end of the range is entered only once. The numbers shown in the table refer to the papers mentioned in the text and are listed in the general references; sets of results denoted in the table by a letter are quoted in papers not specifically mentioned in the text and these are listed separately. There is some overlap of the references quoted here with those quoted by Faber and Ziman; in particular some of the earliest work is not listed here. Further references to density measurements can also be found in two AERE publications: the "Compendia of References to Studies of the Properties of Liquid Metal Binary Systems which relate to their Structure" by Mott, Downey and Cumming [A2] and Mott [A3]. Again some overlap occurs between the density measurements referred to by Mott *et al.* and those listed in this table. It is suggested that a reasonably complete picture of density work on liquid metal binary systems, from which nothing of significance up to 1970 has been omitted, can be obtained by reading this table in conjunction with that of Faber and Zimam, together with the Compendia by Mott *et al.*

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The following references relate to density measurements on liquid binary alloys systems, which are summarised in

TABLE II Summary of the reported density measurements on most common binary alloy systems. This summary is regarded as being reasonably comprehensive up to the end of 1970.

Solute ↓ / Solvent →	Cu	Ag	Au	Mg	Zn	Cd	Hg	Al	Ga	In	Sn	Pb	Sb	Bi	Tl	Ce	Li	Na	K	Ni	Te	Se
Cu		h,v	h,v		e,t,C			14,u,x,B			14,16	22,54,m	e	n		29				z		
Ag	h,v		15								49,50	55	y	55,C								
Au	h,v	15																				
Mg								i,B			k,D,F	k,D,E		D	E,G	k						
Zn	e,t,C			j		26,a	57,a	e,B,C		a	43,26,a,g		26,f,E					p				
Cd					26,a		57,a			28	26,28,g	26,28,g	31,32,D	26,28	28		p					
Hg										27,36,52,J	36								L			
Al	14,x,B			i,B	e,t,B,C								f,B									
Ga										b	b	b,c										
In					a	28	27,36,52,57,d,J		b		b	b,c		b	b						E	
Sn	14	49,50	36	A,D,F	26,43,a,g	26,28,g	36,57,a		b	b,c		16,32,41,52,53,H		26,51,52							E	
Pb	22,54	55		A,D,E		26,28,g				b,c	16,32,41,52,53,H		31,S	26,a,c,K								
Sb	e	y			26,f,E	31,32,D		f,B				31									D,F	
Bi	z	55,C		D		26,28				b	26,51,52	26,a,K			52	29					E,G	
Ni											16	12		o								
Tl				E,G		28				b	52	52		52		29						D
Co																29						
Mn								H						r								
Li					p	p	w					q										
Na					p		57,w					r							D,L			
K																		D,L				
Si				A																		
Ce				k																		
Te											E		E	D,F								
Se															D							
As																					E	

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