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ADA278517

Density of Solids and Liquids

by Peter Hidnert and Elmer L. Peffer

National Bureau of Standards Circular 487
Issued March 15, 1950

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Thermal Expansion of Solids

Ten methods for determining thermal expansion of solids are given in this new Circular, which presents the procedures used to obtain expansion equations and coefficients of expansion of materials. Some applications of thermal expansion are indicated.

Relationships between thermal expansion, temperature, chemical composition, density, compressibility, specific heat, melting point, atomic weight, and other properties of materials are discussed.

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Preface

Density is one of the significant physical properties of materials that is important in science and industry.

This Circular is issued to supply a demand for information about various methods for determinations of the densities of solids and liquids. The Circular also indicates that density determinations may be used to identify materials, and to obtain relationships between density, chemical composition, thermal and mechanical treatments, etc.

This Bureau has published during the past four decades the results of investigations on the densities of various materials. A list of these publications will be sent upon request to anyone interested.

E. U. Condon, *Director*.

Contents

Density of Solids and Liquids

by **Peter Hidnert and Elmer L. Peffer***

Density data may be used for obtaining relationships between density, chemical composition, thermal and mechanical treatments of materials, etc. This circular defines density and specific gravity, describes 11 methods (hydrostatic weighing, picnometer, flotation, hydrometer, falling drop, balanced column, Boyle's law, electromagnetic, elastic helix, ice calorimeter, and volumetric) for determinations of the densities of solids and liquids, and indicates the accuracy of various methods.

I. Introduction

1. Definitions and Terms

Density is a significant physical property of materials, and is important in science and industry. The extensive literature on density shows that determinations of the density of materials is a constant and recurrent problem. For example, density determinations may be used to identify materials, and to obtain relationships between density, chemical composition, thermal and mechanical treatments of materials, etc.

In any list of the physical properties of a substance, its density or specific gravity is usually included. If the values of the density of a substance are to be relied upon when obtained by different observers or by different methods, it is important that they be both accurate and comparable.

Density is the mass per unit volume and is usually expressed in grams per cubic centimeter (or per milliliter)[1] at some definite temperature.

Specific gravity is an abstract number expressing the ratio of the weight of a certain volume of the material in question to the weight of the same volume of some other substance taken as standard at a stated temperature. Water is usually used as the standard substance. Both the temperature of the material and the temperature of the standard substance should be indicated.

Density and specific gravity, while fundamentally different, are nevertheless determined in the same way and may have the same numerical values. The two terms are often used synonymously as expressing the "heaviness" of a substance. Care must be taken, however, to state the units employed and the temperatures involved, otherwise there is danger of confusion and misinterpretation of results.

Specific gravity may be determined at any convenient temperature and referred to water at any desired temperature. For example, specific gravity may be determined at 20° C and referred to water at 20°, 15°, 4° C, or any other temperature. It is then expressed as specific gravity at 20°/20° C, 20°/15° C, or 20°/4° C. If determined at 25° C, the specific gravity is expressed as 25°/20° C, 25°/15° C, or 25°/4° C.

Specific gravity is often expressed in terms of water at the same temperature as that at which the substance is weighed; for example, 15°/15° C, 20°/20° C, or 25°/25° C. It is preferable, however, especially in the case of liquids, to express all specific gravities in terms of water at 4° C. The values are then directly comparable, since they are measured in terms of the same unit, and if the change of specific gravity per degree change of temperature is known they may all be easily reduced to the same temperature. There is also the additional advantage that specific gravities when so expressed are numerically the same as densities in grams per milliliter. For example, specific gravity at 20°/4° C is numerically the same as density at 20° C expressed in grams per milliliter. This is obvious, since, by definition, 1 milliliter of water at 4° C weighs 1 gram.

In making specific gravity determinations on a series of samples of the same kind, it is likely that the temperatures of the various samples will differ somewhat unless a constant temperature bath is used. Suppose the temperatures range as follows: 23.5°, 24.4°, 25.0°, 25.6°, and 26.2° C. The specific gravities may then be calculated at 23.5°/4°, 24.4°/4°, 25.0°/4°, 25.6°/4°, and 26.2°/4° C, and, if the change of specific gravity per degree centi-

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*Deceased.

[1] The cubic centimeter (that is, the volume of a cube 1 cm on a side) is not equal to the milliliter, but the difference is so slight as to be negligible in all ordinary determinations. The milliliter is equal to 1.000028 cubic centimeters. In volumetric measurements the unit of volume usually employed is the milliliter (ml), though it is sometimes erroneously referred to as the cubic centimeter (cc). When the cubic centimeter is actually intended it should be written "cm³" and not as "cc". The cubic centimeter is usually employed to express volumes calculated from linear measurements.

grade is known, the values can at once be reduced to 25°/4° C by multiplying the change per degree centigrade by the difference between the temperature of observation and 25° C. For example, if the samples are linseed oil, of which the change in specific gravity is 0.00068 per degree centigrade, the specific gravities can be reduced to 25°/4° C by subtracting from the observed values of the successive samples 0.00068 times 1.5, 0.6, 0.0, −0.6, and −1.2.

If the above specific gravities had been expressed in terms of water at the temperature of observation, they would have been at 23.5°/23.5°, 24.4°/24.4°, 25.0°/25.0°, 25.6°/25.6°, and 26.2°/26.2° C, and would not then have been directly comparable or easily reducible to the same basis, since the correction to be applied in each case would then involve both the expansion of the sample itself and the change of the unit of measurement, that is, the density of water.

For purposes of comparison, specific gravities are sometimes shown in parallel columns at 15°/15° and at 25°/25° C. This method does not make possible a real comparison since the values given in the two columns are measured in different units. It shows only the difference between the expansion of the sample in question and that of water over the same temperature range. If it should happen that the sample in question had the same rate of expansion as water then the specific gravities of the sample at 15°/15° and at 25°/25° C would be identical, that is, it would appear that the specific gravity of the sample did not change with change of temperature.

In all determinations one should distinguish between apparent and true specific gravity. In case the true specific gravity is desired, this can be obtained either by correcting all weighings for air buoyancy before determining the ratio of the weights, or by applying a correction to the apparent specific gravity.

Table 1 [1][2] gives corrections to be applied to apparent specific gravities in order to obtain true specific gravities. These corrections are based on specific gravities at 25°/25° C, but they are sufficiently accurate for practical purposes at ordinary laboratory temperatures. For substances having specific gravities that do not differ much from unity, the difference between apparent and true specific gravity is small, but for substances with specific gravities far from unity, the difference between apparent and true specific gravity is correspondingly large.

In case it is desired to correct the apparent weight of a body for air buoyancy, this correction may be calculated by means of an appropriate table of air densities at various temperatures and pressures. The buoyancy correction to be added to any apparent weight, to reduce it to true weight in vacuum, is calculated by multiplying the air density by the difference in volume between the body weighed and the weights required to balance it on an even arm balance, or

$$B=\rho(V-V_w), \tag{1}$$

where B is the air buoyancy, ρ the air density, V the volume of body weighed, and V_w the volume of weights.

Table 1. *Corrections to be applied to apparent specific gravities in order to obtain true specific gravities at 25°/25° C (U. S. Pharmacopoeia)*

Apparent specific gravity	Correction	Apparent specific gravity	Correction
0.6	0.00047	2.0	−.00118
.7	.00035	3.0	−.00236
.8	.00024	4.0	−.00353
.9	.00012	5.0	−.00471
1.0	.00000	6.0	−.00589
1.1	−.00012	7.0	−.00706
1.2	−.00024	8.0	−.00824
1.3	−.00035	9.0	−.00942
1.4	−.00047	10.0	−.01060
1.5	−.00059	11.0	−.01177
1.6	−.00071	12.0	−.01295
1.7	−.00082	13.0	−.01413
1.8	−.00094	14.0	−.01530
1.9	−.00106	15.0	−.01648

The numerical values of V and V_w can be arrived at by an approximation which may be carried to any desired degree of accuracy. The value of V may be obtained from the relation

$$V=\frac{m}{d}, \tag{2}$$

where m is the mass, and d is the density of the body. For a first approximation m may be taken as the uncorrected weight, and d as the apparent density. In the same way V_w may be taken as the apparent weight divided by the assumed density of the weights (8.4 for brass weights). This gives an approximate value for B which may be applied to the apparent weights and by this means a more exact value for V and V_w can be determined and with these values of V and V_w a more exact value of B can be obtained. This process may be continued until the successive values of V, V_w, and B differ by negligible amounts. In most cases the second approximation will be found to be sufficiently exact, and in many cases, only the first approximation will be required.

The weight of a body in vacuum may also be computed from the equation

$$\begin{aligned} M&=W+\rho\left(\frac{M}{d_1}-\frac{W}{d_2}\right)=W\frac{d_1}{d_2}\left(\frac{d_2-\rho}{d_1-\rho}\right)\\ &=W\frac{d_1}{d_1-\rho}\left(1-\frac{\rho}{d_2}\right)=W\left[1+\frac{\rho}{d_2}\left(\frac{d_2-d_1}{d_1-\rho}\right)\right]\\ &=W+\frac{kW}{1000}, \end{aligned} \tag{3}$$

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[2] Figures in brackets indicate the literature references at the end of this Circular.

where M is the weight of body in vacuum, W the apparent weight of body in air, ρ the density of air, d_1 the density of body, d_2 the density of weights, and k the correction factor. Table 2 gives correction factors for $\rho=0.0012$ (dry air at 21° C and 760 mm pressure).

The weighings are reduced to vacuum by means of a special device originally designed for use in correcting weighings of water in tests of volumetric apparatus. This device consists of a glass bulb of such volume that, when suspended from one arm of a balance and counterpoised against a brass weight of equal mass, the number of milligrams that must be added to the pan from which the bulb is suspended to secure equilibrium is equal to the air buoyancy on a liter of water weighed against brass weights. This buoyancy constant when divided by 881.3 ml (the difference in volume between the glass bulb and the brass weights) gives the air density. The bulb is suspended in a glass case to protect it from disturbing air currents. Correction is made for the difference in temperature between this case and the balance where density determinations are made. The density of the brass weights for the purpose of correcting for displaced air is assumed to be 8.4 g/cm^3.

If greater precision is required, the true value for ρ depending on temperature, humidity, and pressure, should be substituted in eq 3. Values for ρ for dry air containing 0.04 percent of CO_2 at various temperatures and pressures may be obtained from table 29 of a previous Bureau Circular [2].

Table 2. *Correction factors (buoyancy) for $\rho=0.0012$*

[BS Circular 19, 6th ed.]

Density of body weighed	Correction factor, k			Density of body weighed	Correction factor, k		
	Pt-Ir weights $d=21.5$ g/cm^3	Brass weights 8.4	Quartz or Al weights 2.65		Pt-Ir weights $d=21.5$ g/cm^3	Brass weights 8.4	Quartz or Al weights 2.65
g/cm^3				*g/cm^3*			
0.5	2.35	2.26	1.95	5.0	0.18	0.10	−0.21
.6	1.95	1.86	1.55	6.0	.15	.06	−.25
.7	1.66	1.57	1.26	7.0	.12	.03	−.28
.8	1.45	1.36	1.05	8.0	.10	.01	−.30
.9	1.28	1.19	0.88	9.0	.08	−.01	−.32
1.0	1.14	1.06	.75	10.0	.06	−.02	−.33
1.1	1.04	0.95	.64	11.0	.05	−.03	−.34
1.2	0.94	.86	.55	12.0	.04	−.04	−.35
1.3	.87	.78	.47	13.0	.04	−.05	−.36
1.4	.80	.72	.40	14.0	.03	−.06	−.37
1.5	.74	.66	.35	15.0	.02	−.06	−.37
1.6	.69	.61	.30	16.0	.02	−.07	−.38
1.7	.65	.56	.25	17.0	.01	−.07	−.38
1.8	.61	.52	.21	18.0	.01	−.08	−.39
1.9	.58	.49	.18	19.0	.01	−.08	−.39
2.0	.54	.46	.15	20.0	.00	−.08	−.39
2.5	.42	.34	.03	21.0	.00	−.09	−.40
3.0	.34	.26	−.05	22.0	.00	−.09	−.40
3.5	.29	.20	−.11	23.0	.00	−.09	−.40
4.0	.24	.16	−.15	24.0	−.01	−.09	−.40

II. Types of Apparatus for Density Determinations

Eleven methods for determinations of the densities[3] of solids and liquids will be described. Free use has been made of publications of many authors, particularly those of the National Bureau of Standards. In order to conserve space it is necessary to omit descriptions of some variations and modifications of the density methods described in this Circular. Some of the illustrations were redrawn with minor changes in order to conform with this Bureau's editorial policy.

1. Hydrostatic Weighing Method

The hydrostatic weighing method may be used for determining the density of solids and liquids.

(a) Solids

For the determination of the density of a solid it is first weighed in air, and then weighed while suspended in a liquid of known density. This is done by attaching one end of a silk thread or fine wire to one arm of an equal arm balance and the other end of the thread or wire to a small basket in which the solid sample is placed. It is necessary to have the thread or wire pass through the surface of the liquid with the basket attached in taking the balance reading before the solid sample is placed in the basket in order that errors due to the weight of this attachment and to the effect of surface tension of the liquid on the suspension thread or wire may be avoided. A fine wire is preferable to a silk thread since large errors may be introduced on small samples by the use of the latter.

The density of the solid sample is computed from the weight in air divided by its volume. This volume is equal to the loss of weight of the sample divided by the density of the liquid at the temperature of observation.

(b) Liquids

The density of a liquid may be determined by weighing in the liquid a sinker of known mass and volume. The arrangement of apparatus used at the National Bureau of Standards is shown in figures 1 to 4. The densimeter tube containing

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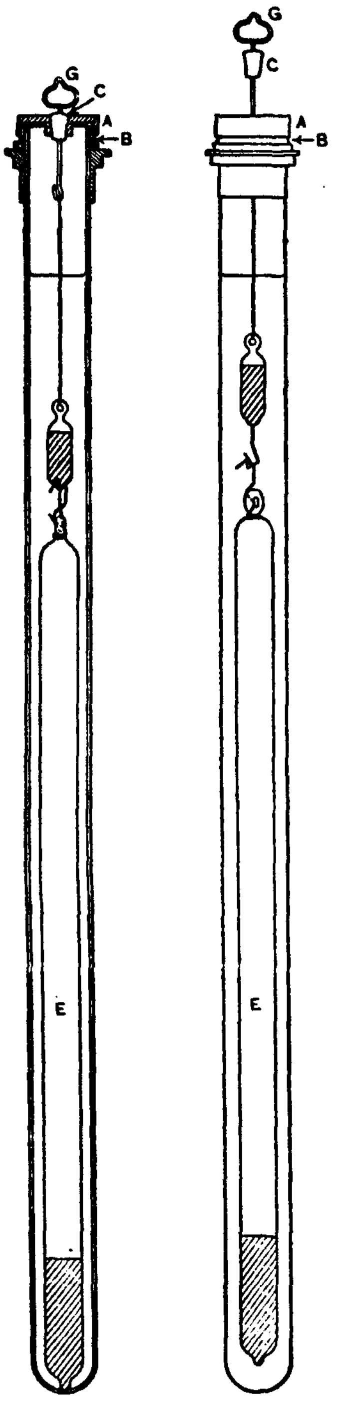
[3] At the request of the American Society for Testing Materials, the National Bureau of Standards completed in 1941 an investigation of instruments available to industry for the determination, indication, or recording of the specific gravities of gases. Eleven different instruments were investigated with the use of 15 test gases of known specific gravities. Determinations were made of the accuracy and reproducibility, of the effects of changes of temperature, relative humidity and water content of the surrounding air, and of sources of error and applicable corrections. The test gases ranged in specific gravity from helium (0.15), in steps of approximately 0.15, to butane (2.06). The probable errors in the values of the specific gravities of the test gases and mixtures used as reference standards averaged ±0.00004, which made it possible to fix the errors of the instruments to 0.0001 specific gravity unit. The results of this investigation have been published by Smith, Eiseman, and Creitz [3].

the liquid and the immersed sinker *E* is shown in figure 1. A special cap is used for closing the densimeter tube when weighings are not being made. This cap consists of a brass cover, *A*, fitted to the tube by a soft rubber bushing, *B*. Through the center of the cover is a hole, which may be closed by a tightly fitting brass plug, *C*. To the upper and lower faces of this plug is attached the suspension wire. When weighings are in progress, the suspension is as shown in figure 1, b, access of the outer air being only through the hole in the cap. When weighings are not in progress, this hole is closed by the plug, as shown in figure 1, a, to avoid changes in concentration of the liquid, caused by evaporation or by absorption of water vapor from the air. In figures 2 and 3 the densimeter tube, *H*, is shown fixed in place in the inner water bath.

The water in the inner bath is kept in constant circulation by the propeller *I*. This bath is immersed in an outer bath kept in constant circulation by means of a motor-driven propeller,



a b

Figure 1. *Densimeter tube, one-third size (Osborne).*

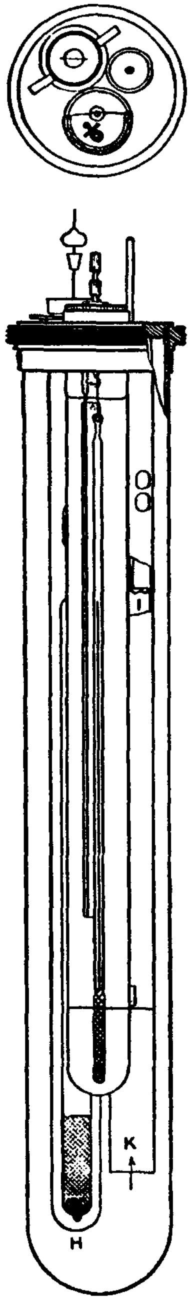


Figure 2. *Densimeter tube H in inner water bath, one-fourth size (Osborne).*

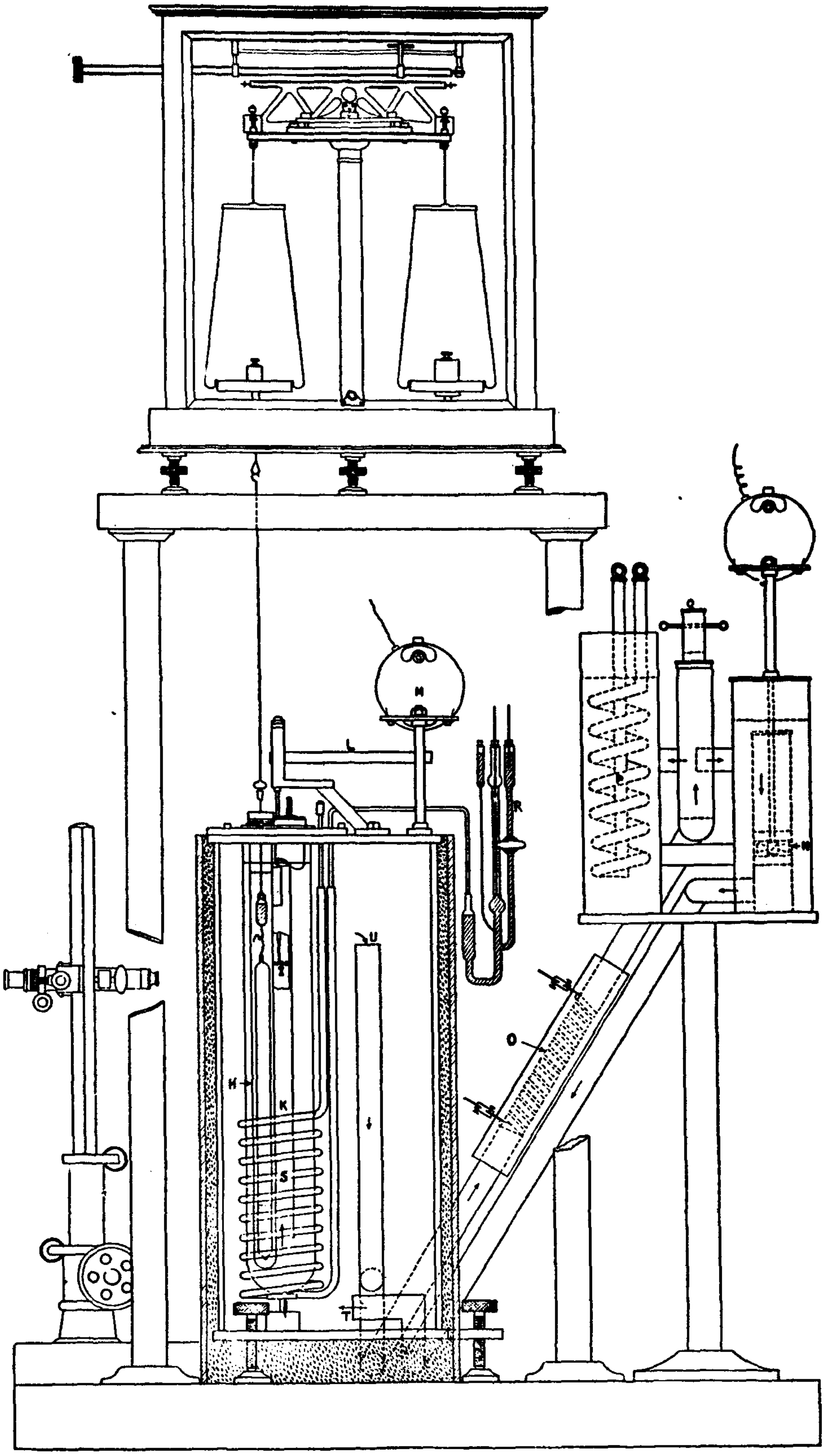


Figure 3. *Apparatus for determination of density by hydrostatic weighing method, one-ninth size* (*Osborne*).

N, placed outside the bath. The temperature of this outer bath is maintained constant or changed at will by means of the electric heating coil, *O*, surrounding the return pipe and by the tubular coil, *P*, connected with a refrigerating unit maintained at a temperature below 0° C. The flow of cooled liquid in this coil is adjusted by means of a valve. By means of special valve, *Q*, the flow of water in the circulating apparatus may be directed entirely through the cooling chamber, directly through the circulating propeller, or divided, part going either way at will, thus regulating the quantity of heat removed from the system by the refrigerating unit. The cooling is made slightly in excess of the heat acquired from the surrounding air and that produced by the circulation, the balance being maintained by means of the heating coil.

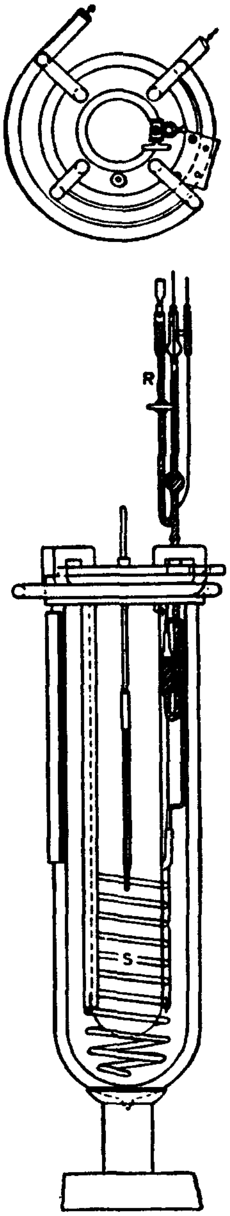


FIGURE 4. *Bath for use in determination of density by hydrostatic weighing method, one-eighth size (Osborne).*

This coil, which has a resistance of 10 ohms, is made of Chromel A or Nichrome V ribbon, wound over mica on the brass tube through which the return flow takes place. It is used both for regulation of temperature and for rapid heating when changing the temperature. For regulation it is connected in series with a variable resistance consisting of a sliding contact wire rheostat and a bank of parallel connected lamps. Another lamp bank is connected as a shunt on this variable resistance in the circuit of which is a relay operated by a thermoregulator, *R*. The bulb of this thermoregulator is the tubular copper coil *S*, containing about 20 ml of xylol.

A rise in temperature closes an electric circuit, the relay is thus energized, the shunt circuit broken, and the current in the heating coil diminished. When the temperature falls sufficiently, this action is reversed. The sensitivity of the regulation varies with conditions. Under the most adverse conditions the regulating energy used in the heating coil is from 100 to 140 watts and maintains the outer bath constant within 0.05 deg C. Under the best conditions the energy varies from 10 to 20 watts, keeping the temperature of the bath constant within 0.01 deg C. The periodic variation in temperature of the outer bath is in either case far too rapid to produce any perceptible change in the inner bath. For rapid heating, the small regulating current is replaced, using a double-throw switch, by a heavier current supplying about 1,500 watts in the heating coil.

The outer bath as first arranged is shown in figure 3. It was contained in a rectangular tank with plate-glass walls and brass bottom and top. The insulation consisted of cotton between two layers of heavy cardboard. The water entered at *T* and left at *U*, thus insuring complete circulation. Owing to the repeated difficulty on account of leakage of the joints, this tank was replaced by a double-walled glass cylindrical vacuum jacket as shown in figure 4. The top was closed by a brass cap cemented to the glass. The water enters by two tubes extending to the bottom and leaves by two tubes at the top. The greatest difficulty with this container for the outer bath was the distortion of the image of the thermometers, owing to the cylindrical surface of the container. This difficulty was remedied to a considerable extent by cementing a plane glass plate to the outside surface of the container, forming a cell which when filled with water corrected most of the aberration. The cylindrical container is covered with nickeled paper or aluminum foil in order to exclude or minimize radiation. Windows are cut in the paper or foil to permit observations to be made.

The temperatures are observed on two mercury ermometers [4] suspended in a tube of water, the sition of which is symmetrical in the inner bath that of the densimeter tube. The thermometers e so mounted on a movable cap that by its tation they may be successively brought into sition for reading. They are read with the aid a long-focus microscope so mounted as to be ovable vertically. The object of placing the ermometers in a tube instead of directly in ntact with the water of the inner circulating th is to eliminate, as far as possible, errors due temperature lag within the densimeter tube. nce the liquid sample is separated from the rculating bath by the densimeter tube, the ermometers should be separated from the circu- ting bath by a similar tube so that when a nstant temperature is indicated by the ther- ometers the same constant temperature shall tain within the densimeter tube.

The apparatus shown in figures 1 to 4 and scribed above has now been modified in several spects. The tubular copper coil, *S*, has been placed with a sinuous glass tube having vertical gments. Thermocouples have been placed in e outer and inner baths and in the thermometer be to detect small temperature changes.

A sinker made of annealed Jena 16^{III} glass, llasted with mercury, is used. Its volumes are lculated from its weight in vacuum and its ap- arent weights in twice distilled water at various mperatures, using known values for the density water [2, 5]. The sinker should have a volume 50 to 100 ml.

The sinker is suspended by a hook from a small condary sinker attached to a wire let down from ne pan of a balance as shown in figure 3. The condary sinker has a mass sufficient to keep the spension wire straight and in its proper position, nd is always immersed in the liquid, whether the rger sinker (of known mass and volume) is tached or not.

The platinum suspension wire passing through e surface of the liquid sample, has a diameter [5] 0.2 mm and is covered with a fine layer of npolished gold by electrodeposition. In the se of liquids which imperfectly wet the suspen- on wire, this roughening of the surface of the ire is essential, but with such liquids as linseed l and turpentine it is probably unnecessary.

The weighings are made on a sensitive balance y the method of substitution, that is, a constant ass is kept on one pan of the balance and the eighings made on the other pan. Sufficient eights are placed on the latter pan to secure quilibrium, first with the sinker attached and en detached. The weights were calibrated in rms of known standards and were accurately djusted, so that the maximum error of any possible combination of weights is so small in comparison with accidental errors as to be negligible.

In making density determinations of a liquid by the hydrostatic weighing method, the procedure is as follows:

The water in the outside circulating bath is brought to the desired temperature and, before observations are begun, sufficient time is allowed to elapse for the apparatus to reach the steady state. When the thermometers in the inner tube indicate a constant temperature it is assumed that the liquid in the densimeter tube is at the same constant temperature and observations are begun. First, a weighing is made with the sinker suspended in the liquid sample, then the temperature is observed on each of two thermometers; next, a weighing is made with the sinker off, then a second weighing with the sinker on, and after that a second observation of temperature. The temperature may then be changed to a different temperature and the same procedure followed.

The density of the liquid sample is calculated by means of the equation

$$D_t = \frac{W - \frac{(w-w_1)+(w-w_2)}{2}\left(1-\frac{\rho}{d_w}\right)}{V_t}, \qquad (4)$$

where D_t is the density of liquid sample at temperature t, W is the weight of sinker in vacuum, w is the weighing with sinker off, w_1 and w_2 are the weighings with sinker in the liquid, ρ is the air density, d_w is the density of weights (8.4 is usually assumed for brass weights), and V_t is the volume of sinker at temperature t.

With this method it is possible to obtain densities of ordinary liquids that are accurate to within 2 units in the fifth decimal place. However, Redlich and Bigeleisen [7] and Prang [4] claimed an accuracy of approximately 4 units in the seventh place and 4 to 5 units in the eighth place, respectively.

Additional information about the hydrostatic weighing method used at the National Bureau of Standards is given in publications by Osborne [8], Bearce [9], and Bearce and Peffer [10]. Wirth [11], Prang [4], Schulz [6], and Redlich and Bigeleisen [7] also described the hydrostatic weighing method used by them for determinations of the densities of liquids.

The Westphal balance indicated in figure 5 is a direct-reading instrument for determinations of the density of liquids by hydrostatic weighing. The balance consists of a pivoted beam graduated on one arm from which is suspended a sinker by means of a fine platinum wire. The movable weights (riders), in terms of density, represent units, tenths, hundredths, thousandths, and ten-thousandths. The Westphal balance should be in equilibrium when the sinker is suspended in water at a given temperature and the unit weight is in

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Prang [4] used a copper-constantan differential thermoelement for deter- ning the temperature of a large sinker to within 0.0005 deg C (correspond- to 0.03 mg in weight).

[5] Prang [4] and Schulz [6] used platinum suspension wires 0.05 and 0.02 n in diameter, respectively.

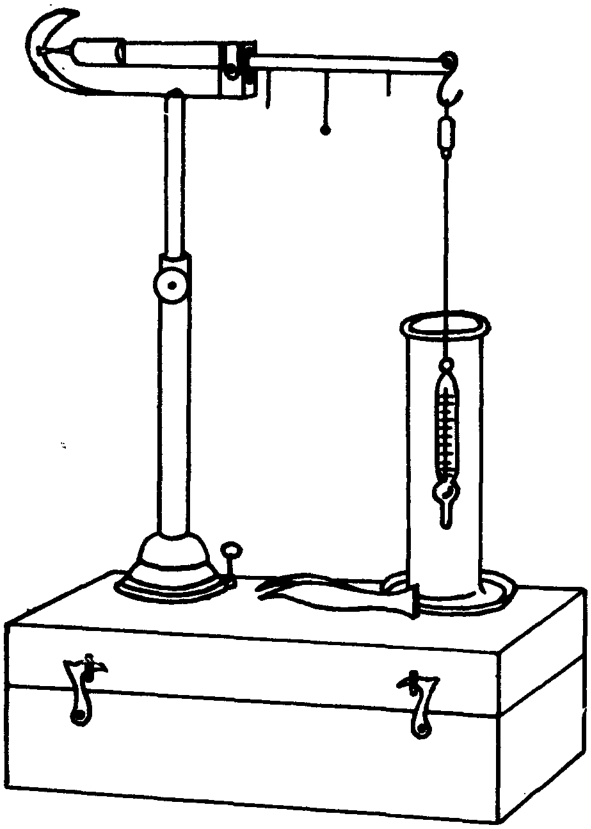

FIGURE 5. *Westphal balance for determinations of the density of liquids (Wright).*

proper position on the beam. When the sinker is suspended in another liquid at the same temperature, different weights may be required to bring the balance to equilibrium. The density is read directly from the values of the weights and their positions on the beam.

The Westphal balance is in general about as accurate as a hydrometer but not as convenient. Its principal advantage is that it can be used on small samples of liquids.

Forziati, Mair, and Rossini [12] described a density balance which is similar in principle to the Westphal balance. They used the balance shown in figure 6 for measurements of the density of purified liquid hydrocarbons and of mixtures of hydrocarbons, on samples as small as 9 ml in volume, with a precision of several parts per 100,000.

The scale on this particular balance ranges[6] from 0.65 to 0.95 g/ml, with the smallest division on the scale corresponding to 0.0001 g/ml and readings with the vernier being made to 0.00001 g/ml.

The balance was calibrated for measurements of density by making observations on a series of seven hydrocarbons for which values of density were determined by the picnometer method, for air-saturated material at 20°, 25°, and 30° C with an estimated over-all uncertainty of ±0.00002 g/ml.

In reducing the scale readings, corrections (from zero to 0.00003 g/ml) were made for slight inequalities in the spacing of the notches on the beam, which inequalities were determined by measurements with known masses hanging from the left arm of the beam as the rider on the beam was moved successively from one notch to another.

As the density of liquid hydrocarbons changes about 0.00001 g/ml for a change in temperature of 0.01 deg C, and as the sensitivity of the balance is 0.00001 g/ml, changes in temperature of the sample under observation in excess of 0.01 deg C will be indicated as changes in the scale readings at balance. For precise work, it is desirable to have thermometric control that produces a maximum variation in the temperature of the sample of not more than 0.01 deg C.

The effect of differences in surface tension of samples of various liquid hydrocarbons, with different forces on the fine platinum wire supporting the sinker, was calculated to be negligible. As the surface tension of hydrocarbons varies in a more or less regular manner with density, the main effect of differences in surface tension in going from hydrocarbons of low density to those of high density becomes incorporated as part of the calibration correction. The net effect of surface tension then reduces to the effect of the difference in surface tension for hydrocarbons of the same or nearly the same density. Examination of published data in the range of density 0.60 to 0.90 indicates that hydrocarbons of the same or nearly the same density have values of surface tension that differ by not more than about 1 dyne/cm. This corresponds to a maximum error of 0.000005 g/ml in density.

2. Picnometer Method

The picnometer method may be used for determining the density of liquids and solids.

(a) Liquids

The hydrostatic weighing method described in the preceding section is applicable only to such liquids as are of sufficient fluidity to allow the sinker to take up a position of static equilibrium when suspended in the liquid. With the more viscous liquids the sensitivity of the balance is greatly reduced and the weighings become more difficult, and of doubtful accuracy. For such liquids it is therefore necessary, or at least desirable, to use some other method. The method usually resorted to is that of the picnometer or specific gravity bottle.

In the construction of a picnometer the elements desired are as follows:

(a) A form adapted to the rapid attainment of the constant temperature of a surrounding bath.

(b) Means of filling with minimum contact of liquid sample with air.

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[6] Other ranges of scale readings may be obtained as required.

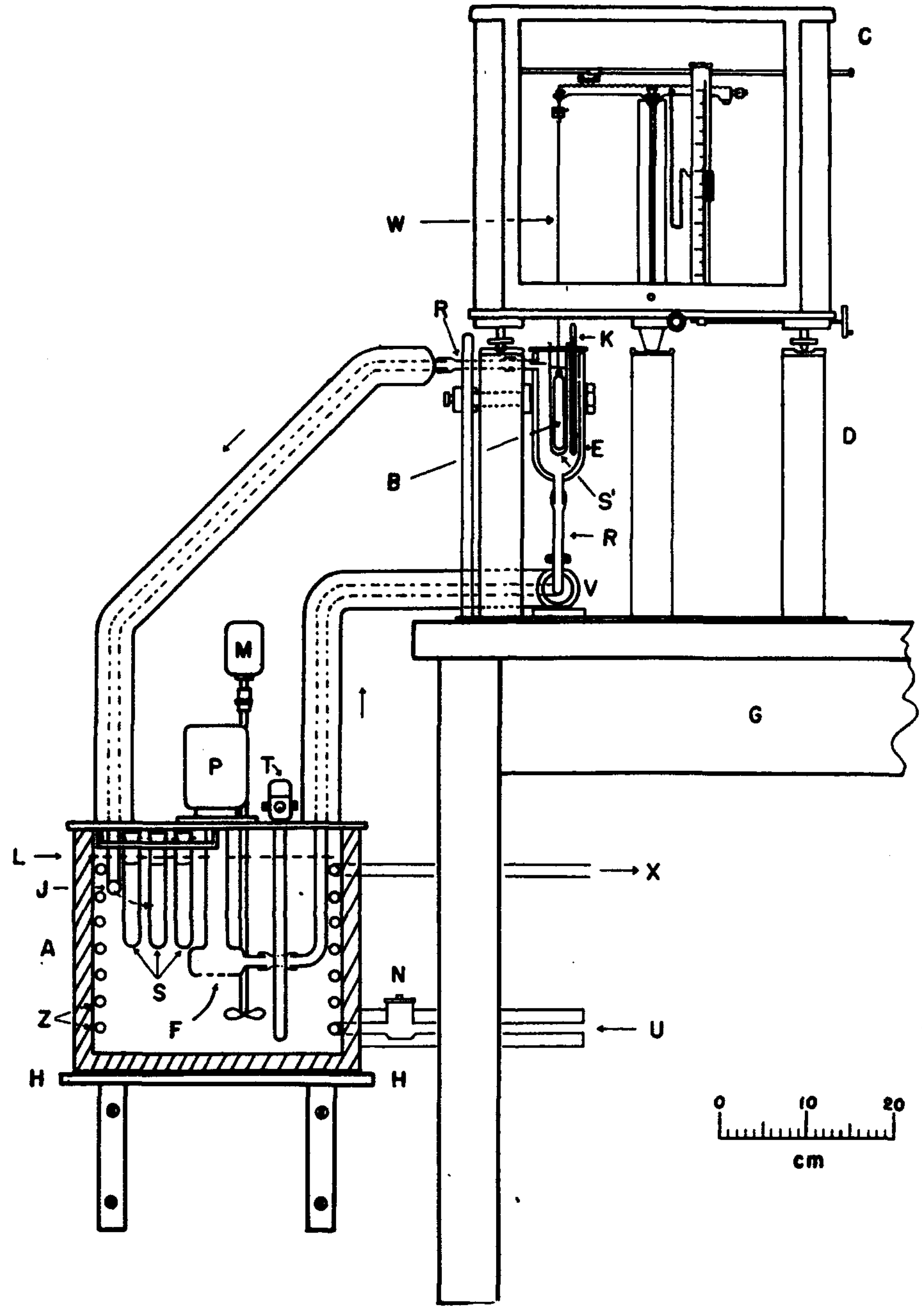

FIGURE 6. *Density balance for determinations of the density of liquids (Forziati, Mair, and Rossini.)*

A, Constant-temperature water reservoir; B, bob or sinker (volume 5 ml); C, chainomatic balance; D, metal supporting stand; E, vacuum-jacketed glass water bath; F, water inlet to pump; G, table; H, shelf (fastened to wall); J, water return from E; K, special mercury-in-glass thermometer (graduated from 19.90° to 20.10°, or from 24.90° to 25.10°, or from 29.90° to 30.10° C, with a sensitivity on the scale of 1 mm equal to 0.05° C); L, level of water; M, motor for stirrer; N, solenoid valve; P, water pump; R, connection of rubber tubing; S,S′, test tubes for containing samples of liquids; T, mercury-type thermoregulator; U, inlet for cooling water; V, valve for controlling flow of water through E; W, platinum wire, 0.003 in. in diameter; X, outlet for cooling water; Z, coil for cooling water.

(c) Protection after filling from change of weight by evaporation or absorption of moisture.

(d) Precision of filling.

Special picnometers on the principle of the Ostwald-Sprengel type have been designed and constructed for use at the National Bureau of Standards [13, 10]. The form of the picnometers is illustrated in figures 7 to 9. They were all made of Jena 16^{III} glass[7] and thoroughly annealed. They are adapted to immersion in the constant-temperature bath described in the preceding section. One of the picnometers (fig. 7) is the

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[7] Pesce and Hölemann [14], Shedlovsky and Brown [15], and Washburn and Smith [16] used picnometers made of fused quartz. The volume of Pesce and Hölemann's picnometer was about 25 cm³, which they claimed could be determined to within 0.0001 cm³ at various temperatures between 25° and 85° C. Washburn and Smith stated that the volumes of their picnometers were determined with an accuracy of 0.1 percent.

Rudolphi [17] form, consisting of a hollow cylinder, which permits a rapid attainment of temperature but at the expense of total volume. Another picnometer (fig. 8) is of the plain cylindrical form. The cap with stopcock attached, as shown in figure 8, is used to control the internal pressure when filling the picnometer. The bulb containing the liquid to be investigated is joined to the picnometer by the ground joint *b*. By proper manipulation, such as inclining the picnometer at a suitable angle and properly varying the air pressure, liquid is introduced into the picnometer after filling, cap *a* is replaced. With the picnometer in position in the water bath, leaving only the upper portions of the capillaries emergent, the adjustment of the quantity of liquid is approximated as the temperature approaches constancy. Liquid may be introduced if necessary by means of a pipette placed with its tip to the aperture of the capillary with proper adjustment of pressure through tube *C*. Small quantities of liquid may be removed by means of a strip of filter paper applied at the tip of the capillary. Enough liquid is removed to bring the meniscus just to the line *e* on the capillary. The inside of the enlargement, *d*, of the tube is dried, either by means of filter paper or by a stream of dry air. The picnometer itself serves as a sensitive thermo-indicator, and until the temperature becomes constant the final adjustment of the quantity of liquid should not be made. When the temperature appears steady, 5 or 10 minutes more are allowed as a margin of safety, and the filling is then completed. The picnometer is closed to prevent evaporation or absorption of moisture by means of cap *f*, shown in figure 7.

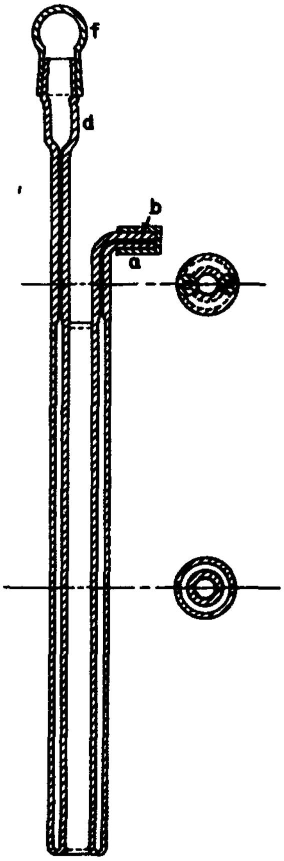

Figure 7. *Picnometer, three-tenths size (Osborne).*

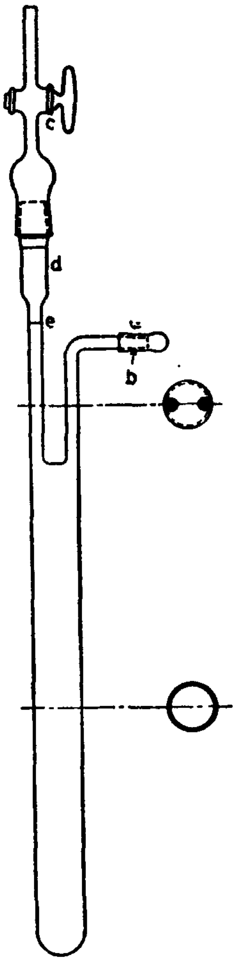

Figure 8. *Picnometer, one-fourth size (Osborne).*

Figure 9 shows a third picnometer used at the National Bureau of Standards. The essential features are tube *E* extending nearly to the lower end of the picnometer, tube *D* extending up through the bottom of reservoir *I*, funnel *G*, and the attachment *F* provided with a stopcock. In filling the picnometer the liquid is placed in funnel *G* and drawn in through *E* by exhausting the air through *F*. By this procedure much time is saved in filling the picnometer, and the method is equally efficient in emptying and cleaning the picnometer when it is desired to introduce another liquid sample. When the filling is completed, *F* and *G* are replaced by caps *A* and *B*, all parts being provided with well-fitting ground joints. The picnometer is then placed in the temperature-control bath and brought to the desired temperature which is recorded. The quantity of liquid in the picnometer is so adjusted that when temperature equilibrium has been established the liquid surface is just flush with the tips of the capillary tubes *C* and *D*. The excess liquid in reservoir *I* is removed and its interior carefully cleaned with the aid of a pipette and filter paper. The picnometer is removed from the bath, and the instrument and its contents are allowed to come to room temperature. The picnometer is dried and then weighed. From the previously determined mass, internal volume, and external volume of the picnometer, and the data obtained for a liquid sample at a given temperature, it is possible to calculate the density of the liquid from the equation

$$D_t=\frac{w\left(1-\frac{\rho}{d_w}\right)+\rho v-P}{V_t}=\frac{M}{V_t} \tag{5}$$

where D_t is the density of liquid sample at temperature t, w is the apparent mass of picnometer filled with liquid sample at temperature t, ρ is the density of air, d_w is the density of weights (8.4 is usually assumed for brass weights), v is the external volume of picnometer, P is the mass of empty picnometer, V_t is the internal volume of picnometer at temperature t, and M is the mass of liquid sample contained in picnometer.

With the picnometers described it is possible to obtain densities of liquids that are accurate to within 1 unit in the fifth decimal place.

Shedlovsky and Brown [15], Robertson [18], and Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg [19] described a picnometer with two graduated capillary tubes of uniform bore, as indicated in figure 10. With this graduated picnometer it is possible to make a density determination of a liquid comparatively quickly for once the picnometer is accurately calibrated the volume of the liquid sample need only be adjusted sufficiently closely to bring the liquid levels somewhere within the graduated regions of the capillary tubes at the temperature in question. After weighing, the picnometer is suspended in a constant-temperature bath provided with a side

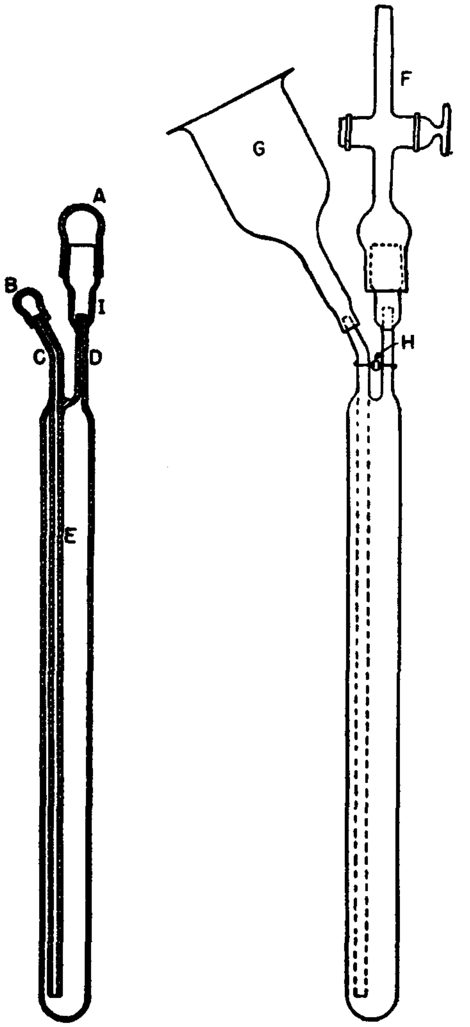

FIGURE 9. *Picnometer (Bearce and Peffer).*

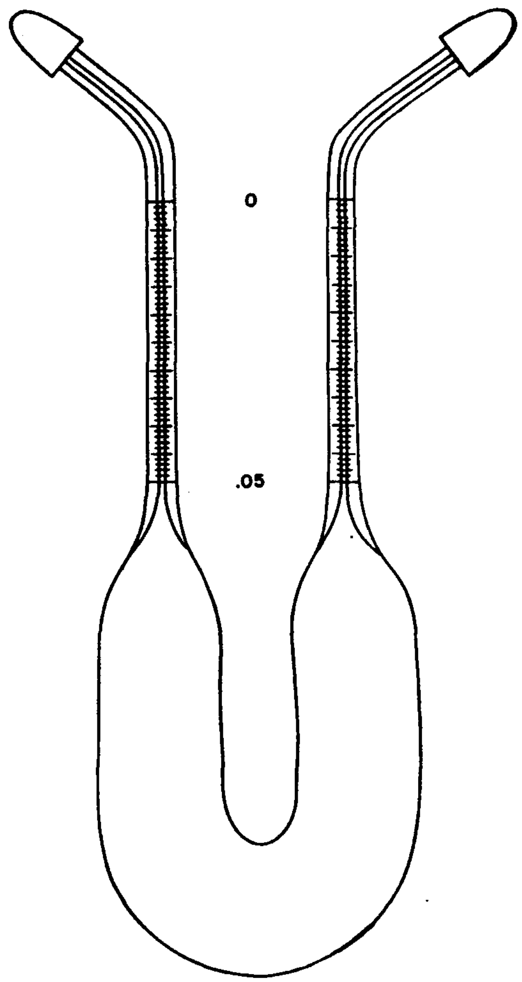

FIGURE 10. *Graduated picnometer (Robertson).*

window through which the meniscus levels can be read with the aid of a lens. The volume of the liquid corresponding to the known weight is thus determined. This picnometer has several obvious advantages over the Sprengel type of picnometer that is commonly used. Besides being more rapid and simpler to use, it avoids two likely sources of error in the Sprengel type, namely, possible variations in the liquid level at the tip and of the temperature in the process of withdrawing the liquid when bringing the meniscus to the reference mark.

Washburn and Smith [16] used a differential picnometer method for determining differences in density of water with a precision of 1 part in 1 million. Two fused-quartz picnometers very closely the same in size and weight, and of the shape shown in figure 11, were used. The capillary stem of each picnometer had a reference mark less than 0.01 cm in thickness, made with a diamond point, and the volume per unit length of the capillary was determined with an accuracy of 0.1 percent by calibration with mercury. The volume of each picnometer up to the reference mark was determined with an accuracy of 0.1 percent by weighing empty, filling with distilled water to any suitable height in the capillary, as read with a cathetometer while the picnometer was in a constant temperature bath, again weighing, and applying a correction for the volume of water in the capillary above the mark.

In making a measurement of the difference in density between a given sample of water and normal water, the first picnometer was filled with normal water and the second with the sample to any suitable heights in the capillaries. The filling was conveniently done with a fine silver capillary and the aid of a low vacuum line, as illustrated in figure 12. The picnometers were then placed side by side, with their ground stoppers loosely in place, in a constant temperature bath containing distilled water and having front and back of plate glass. After thermal equilibrium was attained, the height of the meniscus above the reference mark in each capillary was read with the cathetometer. The picnometers were next taken out of the bath, wiped dry, placed on opposite pans of a balance with their stoppers tightened in place, and the difference in their weights was determined. After the weighing, they were emptied and refilled so that the first picnometer then contained the sample water and the second contained normal water. Again they were placed in the bath in the same positions as before and the capillary heights recorded. They were again taken out, dried, placed on the same balance pans and the second difference in weight determined. The expression for the difference in density is obtained as follows:

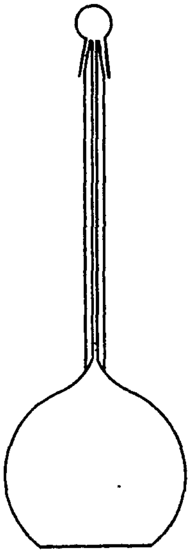

Figure 11. *Fused-quartz picnometer (Washburn and Smith).*

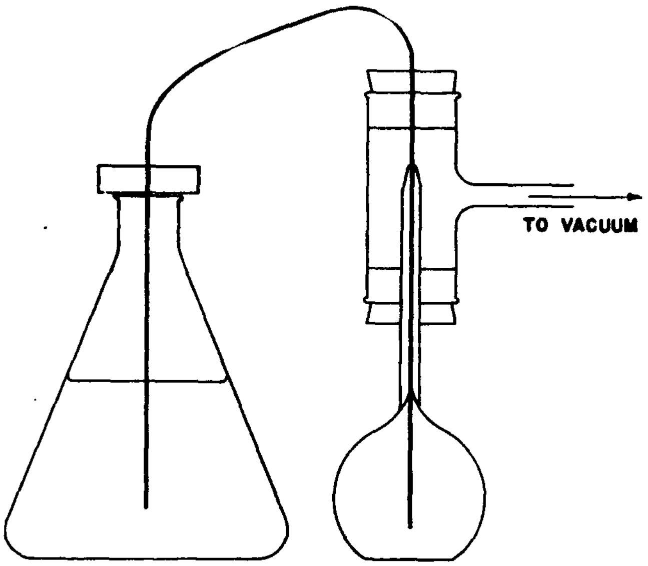

Figure 12. *Device for filling picnometer (Washburn and Smith).*

Let

P_1=weight of picnometer 1
P_2=weight of picnometer 2
V_1=volume of picnometer 1 to the reference mark
V_2=volume of picnometer 2 to the reference mark
D =density of sample investigated
D_0=density of normal water.

$\Delta V_1'$, $\Delta V_1''$, $\Delta V_2'$, $\Delta V_2''$=volume of water above the reference mark in the capillary of picnometer 1 in the first and second fillings and picnometer 2 in the first and second fillings, respectively.

m_1=difference in masses after the first filling
m_2=difference in masses after the second filling.

If picnometer 1 is always placed on the right-hand pan of the balance,

$$P_2+V_2D+\Delta V_2'D=P_1+V_1D_0+\Delta V_1'D_0+m_1 \quad (6)$$

$$P_2+V_2D_0+\Delta V_2''D_0=P_1+V_1D+\Delta V_1''D+m_2. \quad (7)$$

Subtracting eq 7 from eq 6 and rearranging gives

$$(V_1+V_2)(D-D_0)=(m_1-m_2)+(\Delta V_1'D_0-\Delta V_1''D)-(\Delta V_2'D-\Delta V_2''D_0). \quad (8)$$

As this method is used only for the measurement of small differences in density, where $D-D_0<0.001$ g/ml, eq 8 may be written as

$$D-D_0=\frac{(m_1-m_2)+D_0[(\Delta V_1'-\Delta V_1'')-(\Delta V_2'-\Delta V_2'')]}{V_1+V_2}. \quad (9)$$

A bulb volume of about 50 ml and a capillary diameter of about 0.1 cm were found suitable. For a precision in $D-D_0$ of 1 part in 1 million with picnometers of this size, a convenient distribution of precision in the measurements is:

1. The temperature of the stirred water in the bath is held constant to within 0.01 deg C, because with extreme fluctuations of the bath temperature less than 0.01 deg, the lag in the picnometers is sufficient to maintain them constant to within 0.002 deg C.
2. The capillary heights are read to 0.001 cm.
3. The weighings are made to 0.03 mg.

It is advantageous to adjust the capillary heights to make the correction $(\Delta V_1'-\Delta V_1'')-(\Delta V_2'-\Delta V_2'')$ small and thus avoid the necessity for a very precise calibration of the capillaries. It is to be noted that:

1. The dry weights of the picnometers are not required.
2. The two picnometers should be so closely alike that effects of varying humidity are balanced.
3. The temperature of the water in the picnometers should be constant and uniform.
4. The effect of barometric and hydrostatic pressure on the capillary heights is balanced.
5. The (negligible) evaporation past the ground-glass stoppers is balanced.
6. The fused-quartz bulbs should show no measurable temperature hysteresis over the temperature range involved.
7. The small effect of dissolved air is balanced and it is not necessary to prepare air-free water.
8. The correction for air buoyancy affects only the difference of the differences, $(\Delta V_1'-\Delta V_1'')-(\Delta V_2'-\Delta V_2'')$, in the capillary volumes and with proper adjustment of the heights is negligible.

The earliest micromethods for determinations of densities of liquids are based on the use of small picnometers. Capillary tubes are used as containers for small amounts of liquid samples, but these tubes have the disadvantage of being fragile. Micropicnometers of the pipette type are the most practical.

Alber [20] described the two types of micropicnometers shown in figure 13. One type of micropicnometer (fig. 13, a) holds a definite volume, 0.1 ml, and is used in decigram procedures. The other type (fig. 13, b) serves for the measurement of varying volumes according to the amount of sample available and is recommended in two sizes—as a centigram pipette for volumes from 20 to 80 mm³, and as a milligram pipette for volumes from 6 to 16 mm³. The micropic-

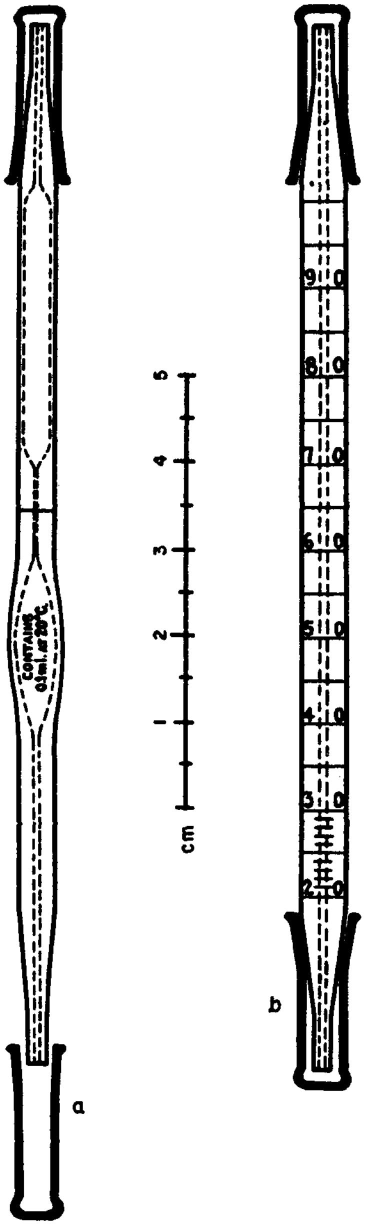

FIGURE 13. *Two types of micropicnometers (Alber).*

a, Decigram pipette, volume 100 mm³; b, centigram pipette if bore=1 mm, volume 20 to 80 mm³; milligram pipette if bore=0.5 mm, volume 6 to 16 mm³.

nometers are equipped with caps, rubber tubing, a mouthpiece filled with some drying agent, and a counterpoise of approximately the same shape and surface (glass rods). Furter [21] described a technique for using a graduated pipette micropicnometer for determinations of the densities of liquids at temperatures up to 300° C.

Other forms of picnometers or modifications of those indicated in this section have been described by Lipkin, Davison, Harvey and Kurtz [22], Newkirk [23], Hall [24], Parker and Parker [25], Scott and Frazier [26], Snyder and Hammond [27], Smith [28], Hennion [29], and Fontana and Calvin [30]. It has been claimed that the most accurate measurements by the picnometer method attain a precision of about 1 part in a million.

(b) Solids

The picnometer method described for liquids may be used in a similar manner for determinations of the densities of solid substances such as powders, crystals, or other solids. For some materials, appreciable errors may be introduced by the expulsion and solution of air and moisture by the picnometer liquid and the adsorption of the picnometer liquid on the surfaces of the materials. The choice of a picnometer liquid depends on the nature of the solid to be investigated. A satisfactory picnometer liquid should have a high degree of wetting power, that is, ability to expel air. The liquid should not combine with or be adsorbed on the surface of the solid and should not dissociate or polymerize during use.

The density of a solid may be computed from the equation

$$D=\frac{dS}{S+P+Vd-W}, \tag{10}$$

where D is the density of solid, d is the density of picnometer liquid, S is the weight of solid, P is the weight of dry, empty picnometer, V is the internal volume of picnometer, and W is the total weight of picnometer, solid, and liquid necessary to fill the picnometer.

With a given picnometer and a liquid of known density, eq 10 becomes

$$D=\frac{dS}{S+k-W}, \tag{11}$$

where k equals $P+Vd$. With this equation it is only necessary to determine the weight of the solid and the total weight of the picnometer, solid, and liquid required to fill the picnometer.

Figure 14 shows 2 small picnometers used by Russell [31] with a centrifuge. The stoppers, which can be made from thick-walled capillary of 0.5- to 1-mm bore, should be very carefully ground in, so that the picnometer volume will be very accurately and reproducibly defined. A fine line encircles the capillary stopper in order to aid in defining the picnometer volume. The picnometer is covered by a cap with a ground-glass joint to prevent any slight evaporation of the picnometer liquid. The volume of the picnometer is determined at the temperatures of use, which in any case should be above the highest balance room temperature that will be encountered. This precaution prevents the picnometer from overflowing and causing a loss of liquid.

Baxter and Wallace [32] used a 25-ml graduated flask, the neck of which was constricted to about 2.5 mm in diameter. For determinations of densities of halogen salts of sodium, potassium, rubidium and cesium, they used toluene for the picnometer liquid. They secured an accuracy in setting of about 0.3 mg of toluene. The neck of the flask was dried before the meniscus was set. Before weighing, the outside of the flask was washed with a dilute solution of ammonia, wiped with a clean, slightly damp, cotton cloth and was allowed to stand in the balance room for at least one hour.

Nutting [33] stated that tetrahydronaphthalene ("tetralin"), dichloroethyl ether ("chlorex"), tetrachloroethane, and the mono-, di- and trichlorobenzenes are quite satisfactory for picnometer liquids in determinations of densities of clays and soils. These liquids are but slightly adsorbed on soil grains, decompose or polymerize very little in use, disturb existing hydrates very slightly if at all, have low vapor pressures, moderate densities, and moderate coefficients of expansion.

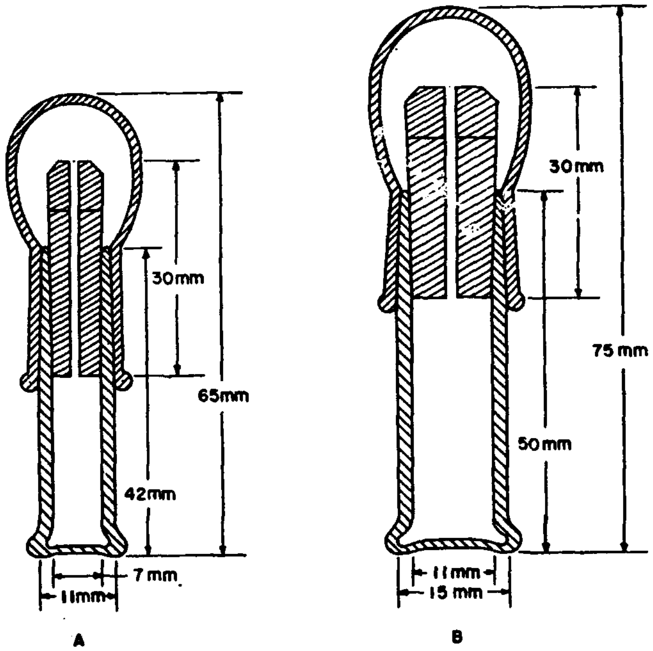

FIGURE 14. *Picnometers for solids (Russell).*

A, Small picnometer, volume about 1 ml; B, larger picnometer, volume about 3 ml.

With the apparatus shown in figure 15, Gooden [34] succeeded in removing air smoothly from fine powder immersed in the liquid of a picnometer, by controlled agitation while the sample is under vacuum. The source of agitation is a vibrator, *V*, of the type used for massaging the face and scalp. A special head, *H*, which holds the picnometer flask, *F*, is used instead of the original vibrator head. This special head consists of a one-hole rubber stopper in which three nails are inserted at a slight angle to grasp the body of the flask. The vibrator is mounted head upward on a heavy base, *B*, which rests on a thick rubber sheet, *G*, covering the top of a wooden block, *W*. The rubber sheet serves as a gasket between the block and a vacuum bell jar, *J*, which covers that part of the apparatus so far described. One or more air holes, *A*, cut in the gasket, prevent the central portion from being lifted when the jar is evacuated. A round-bodied electric lamp cord is run from the vibrator down through the gasket into the block and out at one side, the passage through the wood being bushed airtight with a rubber stopper, *S*. A coupling, *C*, between the vibrator and the gasket may be inserted for convenience in handling.

The following procedure is used by Gooden for adjustment of the vibration intensity and of the pressure reduction: The apparatus is plugged into a continuously variable transformer, *T*, with voltage range from 0 to about 115. The rubber tube from the bell jar to a vacuum line has a branch connected to a manometer, *M*, and another branch left open at the end, *E*. The operator controls vibration and vacuum with one hand on the adjusting knob of the transformer and the index finger of the other hand resting lightly over the tube end, *E*. If it is desired to maintain a particular adjustment for some time without attention, the transformer may be set for the necessary voltage and the vacuum kept fairly constant by leakage through a screw pinchcock, *P*. If the maximum vacuum is desired, the end of a cork stopper may be left resting against *E*.

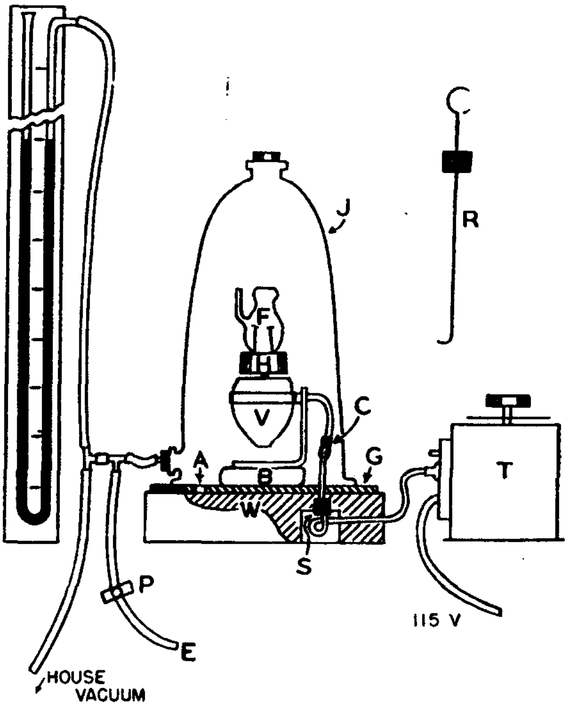

FIGURE 15. *Apparatus for removal of air from samples of powder in picnometer liquid (Gooden).*

Continuous but not violent bubbling until the amount of air remaining does not sensibly affect the volume of the sample, is recommended. A test for completeness of air removal is to observe whether the height of the liquid in the picnometer changes on application or removal of vacuum. If the last significant traces of air are persistent, two methods may be used for hastening their removal. One method is to stir the sample with a stiff wire rod, *R*, extending through a flexible rubber stopper in the top of the bell jar. Another method, which is more convenient, is to jerk the flask repeatedly by jiggling the electric plug that connects the transformer to the electric outlet.

3. Flotation Method

The flotation method of determining the densities of materials may be considered as a development or modification of the hydrostatic weighing method. In the flotation method the object floats in the liquid and no suspension thread or wire is required. Retgers [35] used this method by mixing two liquids until he obtained a mixture in which a submerged solid body floated. The density of the solid body is the same as the density of the mixture which could be determined later by another method.

Pisati and Reggiani [36] were among the earliest investigators to use the flotation method for determinations of the density of liquids.

Figure 16 shows the float used by Warrington [37] for determinations of the densities of liquids. By slipping small ring-shaped platinum weights over the submerged stem, the density of the float may be made to approximate that of the liquid sample. The temperature is then allowed to change very slowly until a temperature is reached at which the float neither sinks nor rises.

The float used by Warrington for determinations of the densities of solids, is indicated in figure 17. He made determinations with the float in water, first with the float loaded with mercury alone, and then with the float loaded with the solid and mercury. The mercury and the solid were in contact with the water. The density of the solid may be computed from the following equation:

$$d_S=\frac{d_M d_w W_S}{W_S d_M+(W_M-W_{M'})(d_w-d_M)}, \qquad (12)$$

where d_S is the density of the solid, d_M is the density of mercury, d_w is the density of water, W_S the weight of solid in vacuum, W_M the weight of mercury required to bring the float to floating equilibrium, and $W_S+W_{M'}$ is the sum of weights of solid and mercury required to bring float to floating equilibrium. Warrington claimed an accuracy of 1 part in 100,000 for densities of solids, and 1 part in a million for liquids.

Richards and Shipley [38, 39] and Richards and Harris [40] used small floats (not exceeding 5 ml volume) of fused quartz, Jena glass, and soft glass, shaped like a buoy or a fish, as illustrated in figure 18. Aging of the floats before calibration and use was found to be important. They found that such floats are easily changed from sinking to rising in aqueous solutions by a fall in temperature of 0.001 deg C near the temperature of floating equilibrium. Their method depends upon noting the precise temperature at which the liquid sample attains the same density as a given, previously calibrated float. This equality of density is indicated when floating equilibrium is attained, that is, when the entirely immersed float neither rises nor sinks in the liquid. Data of a single determination from Richards and Shipley [38] in table 3, indicate that the temperature of floating equilibrium can be determined within 0.001 deg C.

Richards and Shipley used a thermostat capable of maintaining a constant temperature within 0.001 deg C and of easily changing this temperature. The liquid sample is placed in a flask, immersed in a stirred constant temperature bath. The float within the flask is viewed by reflection in a small inclined mirror beneath the water of the bath. Care must be taken to prevent air bubbles from attaching themselves to the float.

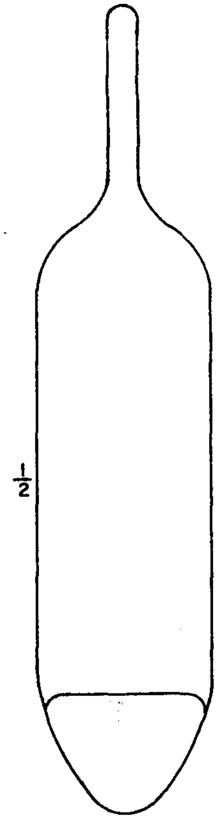

FIGURE 16. *Float for determination of density of liquids, one-half size (Warrington).*

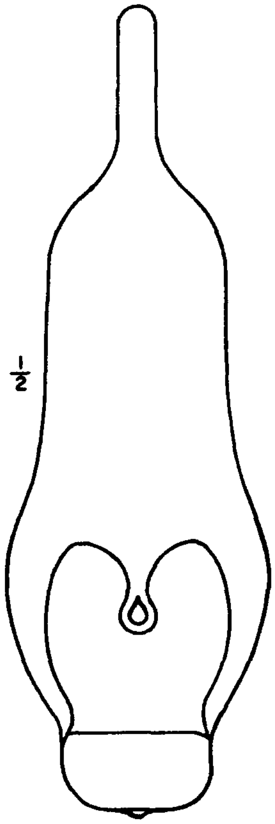

FIGURE 17. *Float for determination of density of solids, one-half size (Warrington).*

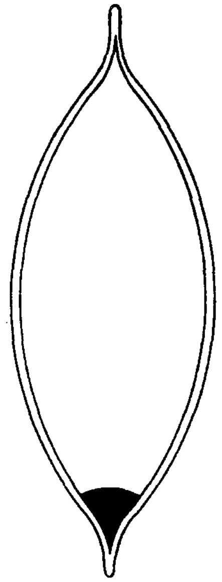

FIGURE 18. *Float for determination of density of liquids (Richards and Shipley).*

Table 3. *Movement of float near temperature of floating equilibrium (Richards and Shipley.)*

Temperature	Movement of float	Temperature	Movement of float
° C		*° C*	
15.394	Sinking.	15.390	Rising.
15.390	Rising.	15.391	Sinking.
15.392	Sinking.		

Figure 19 shows the float used by Lamb and Lee [41] for determinations of densities of aqueous solutions. A piece of soft iron is enclosed in the bulb of the float. By means of an electric current through an external circuit, an electromagnetic attraction is exerted upon the bulb in a vertical direction, in order to obviate the difficulty of varying the buoyancy of the float by small amounts. Lamb and Lee claimed an accuracy of several units in the seventh decimal place.

A fused-quartz float with a cobalt-steel permanent magnet sealed in the bottom of the float was used by Hall and Jones [42]. By slowly reducing the current through a coil the voltage was found which just prevented the float from rising in the liquid sample.

Richards and Shipley varied the temperature of the liquid sample and Lamb and Lee used a magnetic control in order to obtain floating equilibrium in their determinations of densities of liquids. Gilfillan [43] held the temperature of the liquid sample constant at 0° C and altered the buoyancy of the float by varying the hydrostatic pressure. Measurements are made in test tubes connected to a pump and manometer system by means of ground joints. The tubes are kept immersed in a thermostat at 0° C and the movement of the Pyrex-glass float weighted with mercury, is observed through a double-walled evacuated window by means of a telescope.

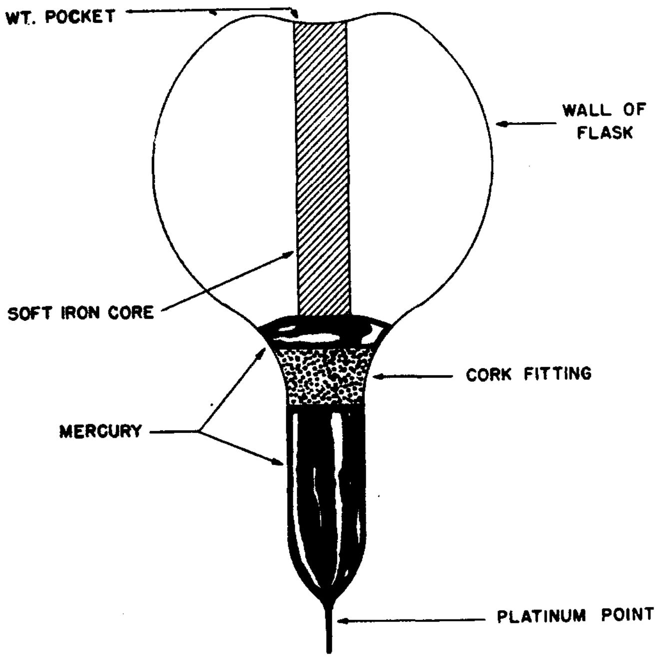

Figure 19. *Float for determination of density of liquids (Lamb and Lee).*

For determinations of the density of small crystals, Bernal and Crowfoot [44] applied the centrifuge in the flotation method. A small quantity of the substance (about 0.05 mg or less) is placed in a suitable liquid contained in a small test tube. Air bubbles are removed from the crystals and liquid by evacuation in a vacuum desiccator. The test tube is then placed in a centrifuge and spun for several minutes at a speed of 2,000 to 4,000 revolutions per minute. A heavier or lighter liquid is added to the tube, according to whether the crystals sink or rise. The process is repeated until the submerged crystals float in the liquid. The density of the crystals is then equal to the density of the liquid, which can be determined by any of the known methods.

Yagoda [45] published a list of organic liquids and solutions of inorganic salts that have been used in density determinations by the flotation method. This list is given in table 4. In adding one liquid to another, it is necessary to choose liquids that are miscible and in which the solid sample is not soluble or is only slightly soluble. The liquids should preferably be colorless or lightly colored, mobile, and not highly volatile.

Table 4. *Liquids used for determinations of density by flotation method (Yagoda)*

Liquid	Specific gravity [a]
ORGANIC LIQUIDS	
Toluene	0.866
Benzene	.879
Carbon bisulfide	1.26
Carbon tetrachloride	1.58
Ethyl iodide	1.94
Ethylene bromide	2.19
Methylene bromide	2.50
Bromoform	2.88
Acetylenetetrabromide	2.97
Methylene iodide	3.33
SATURATED AQUEOUS INORGANIC SALT SOLUTIONS	
Thoulet's solution [b]	3.2
Cadmium borotungstate	3.28
Cobalt borotungstate	3.34
Rohrbach's solution [c]	3.5
Thallium formate at 20°	3.40
Thallium formate at 50°	4.11
Thallium formate at 90 °	4.76

[a] Temperature not indicated.

[b] Contains potassium and mercuric iodides in the molecular ratio of 2:1 (1 part of KI and 1.3 parts of HgI_2 by weight); the salts combining in solution to form the complex K_2HgI_4. By boiling off the excess water until a fragment of fluorite is floated on the surface, a pale amber-colored solution results, with a specific gravity of about 3.2 at room temperature.

[c] Is an analogous complex of barium mercuric iodide (see footnote b).

A procedure for the preparation of a set of floats for use as indicators for determining the densities of liquid or solid samples of materials, has been described by Blank [46]. These floats prepared from glass tubing (1½ cm in length and 1 cm in diameter) and lead foil, may be used for densities from about 1 to 11.

Emeléus and coworkers [47] considered fused quartz as the ideal material for floats because of its small thermal expansion, great elasticity, mechanical strength, permanence and insolubility. They found that a slim cylindrical float is better than a fish-like form, for the movement of the former responds more rapidly and certainly to small differences in the density of a liquid. Their floats were about 75 mm long and 4 mm in diameter and had a ring at the top so that they could be handled conveniently by means of a glass hook.

Additional information about the flotation method is given by Lewis and MacDonald [48], Randall and Longtin [49], Johnston and Hutchison [50], and Hutchison and Johnston [51]. Randall and Longtin described a microfloat of Pyrex glass for determinations of the density of very small samples of water, as small as 0.1 ml. They made floats about the size of a grain of wheat.

4. Hydrometer Method

The hydrometer consists of a graduated cylindrical stem and a bulb weighted with mercury or lead. For a determination of the density or specific gravity of a liquid by this method, it is necessary to use a suitable hydrometer that will sink in the liquid to such position that a part of the graduated stem extends above the surface of the liquid.

Some hydrometers (thermohydrometers) have a thermometer in the stem to indicate the temperature of the liquid. If the thermometer is not made as a part of the hydrometer, the thermometer should be so placed that the bulb can assume the temperature of the liquid, and as much of the mercury column as is feasible should be immersed. This is important, especially if the temperature of the liquid differs greatly from that of the surrounding air. In reading the thermometer accurately, care must be taken that the line of sight is perpendicular to the thermometer scale in order to avoid parallax. The temperature of a liquid should be read to a degree of accuracy that is comparable with the accuracy of the determination of the density of the liquid.

Hydrometers should be made of smooth, transparent glass without bubbles, striae, or other imperfections. The glass should be of a kind that adequately resists the action of chemical reagents and also possesses suitable thermal qualities, such as would adapt it to use for thermometers.

Each section of a hydrometer perpendicular to its axis should be circular. The stem should be uniform in cross section and no irregularities should be perceptible. The outer surface should be symmetrical about a vertical axis. There should be no unnecessary thickening of the glass walls and no abrupt constrictions which would hinder convenient cleaning. The capillary stem of a thermohydrometer should be parallel to the axis and should extend at least 10 mm above the scale. It should contain an enlargement that will permit heating to 120° C.

Before graduation and adjustment all hydrometers should be thoroughly annealed.

Material used for ballast should be confined to the bottom of the instrument, and no loose material of any sort should be inside a hydrometer. The disposition of the weight should be such that the hydrometer will always float with its axis vertical.

Only the best quality of paper should be used for scales and designating labels inside the hydrometer. The paper usually known as first-class ledger paper is suitable for this purpose. The scales and labels should be securely fastened in place by some material which does not soften at the highest temperature to which the hydrometer will be exposed in use and which does not deteriorate with time. The scale should be straight and without twist.

The hydrometer should be perfectly dry on the inside when sealed. Thermometer bulbs and capillary tubes should be free from air.

The hydrometer stem should extend above the top of the scale at least 1.5 cm and below the scale should continue cylindrical for at least 3 mm. The thermometer scale should not extend beyond the cylindrical portion of the containing tube nor beyond the straight portion of the capillary. It is desirable that the thermometer scale should include the ice point (0° C).

The total length of a hydrometer should not exceed 45 cm and should generally be much less than this for the sake of convenience. The top of the stem should be neatly rounded, but not unnecessarily thickened. The graduations and inscriptions should be in permanent black ink, such as india ink. They should be clear and distinct.

The length of the smallest subdivisions of the scales should, in general, be from 1 to 2 mm. The division lines must be perpendicular to the axis of the hydrometer; that is, horizontal when the instrument is floating.

The lengths of division and subdivision lines both on hydrometer and thermometer scales should be so chosen as to facilitate readings. Sufficient lines should be numbered to indicate clearly the reading at any point. The numbers at the ends of the scale intervals should be complete, but those intermediate may be abbreviated.

The division lines of the hydrometer scale should extend at least one-fourth around the circumference of the stem and be adjacent to or intersect a line parallel to the axis indicating the front of the scale. The division lines of the thermometer scale should extend behind and on both sides of the capillary. To facilitate readings near the ends of the hydrometer scale the graduations should be continued a few divisions beyond the ends of the principal interval.

The hydrometer scale for density indications should be divided in 0.001, 0.0005, 0.0002, or 0.0001 unit of the density. For percent or degree indications the hydrometer scale should be divided into whole, half, fifth, or tenth percents or degrees. The thermometer scale should be divided into whole or half degrees.

The hydrometer scale or a suitable special label should bear an inscription that indicates unequivocally the purpose of the instrument. This inscription should denote the liquid for which the hydrometer is intended, the temperature at which it is to be used, and the character of the indication, including definition of any arbitrary scale employed.

Hydrometers are seldom used for the greatest accuracy, as the usual conditions under which they are used preclude such special manipulation and exact observation as are necessary to obtain high precision. It is, nevertheless, important that they be accurately graduated to avoid, as far as possible, the use of instrumental corrections, and to obtain this result it is necessary to employ certain precautions and methods in standardizing these instruments.

The methods of manipulation described below are, in general, employed at the National Bureau of Standards in testing hydrometers and should be followed by the manufacturer and user to a degree depending on the accuracy required.

The hydrometer should be clean, dry, and at the temperature of the liquid before immersing to make a reading. The liquid should be contained in a clear, smooth glass vessel of suitable size and shape. By means of a stirrer which reaches to the bottom of the vessel, the liquid should be thoroughly mixed. The hydrometer is slowly immersed in the liquid and pushed slightly below the point where it floats naturally and then allowed to float freely. The reading on the graduated stem should not be made until the liquid and the hydrometer are free from air bubbles and at rest.

The correct method of reading the hydrometer is illustrated in figure 20. The eye should be placed slightly below the plane of the surface of the liquid (fig. 20, A) and then raised slowly until this surface, seen as an ellipse, becomes a straight line (fig. 20, B). The point at which this line cuts the graduated stem of the hydrometer should be taken as the reading of the instrument (fig. 20, B). The reading gives the density or specific gravity directly or it may be reduced to density or specific gravity by means of an accompanying table.

In case the liquid is not sufficiently clear to allow the reading to be made as described, it is necessary to read from above the liquid surface (apparent reading) and to estimate as accurately as possible the point to which the liquid rises on the hydrometer stem. As the hydrometer is calibrated to give correct indications when read at the principal surface of the liquid, it is necessary to correct the apparent reading above the liquid surface by an amount equal to the height to which the liquid creeps up on the stem of the hydrometer. The amount of this correction may be determined with sufficient accuracy for most purposes by taking corresponding readings in a clear liquid and noting the difference.

In order that a hydrometer may correctly indicate the density of a liquid, it is essential that the liquid be uniform throughout and at the temperature at which the hydrometer was calibrated.

To insure uniformity in the liquid, stirring is required shortly before making the observation. This stirring should be complete and may be well accomplished by a perforated disk or spiral at the end of a rod long enough to reach the bottom of the vessel containing the liquid. Motion of this stirrer from top to bottom serves to disperse layers of the liquid of different density.

The liquid should be at nearly the temperature of the surrounding atmosphere, as otherwise its temperature will be changing during the observation, causing not only differences in density but also doubt as to the actual temperature. When

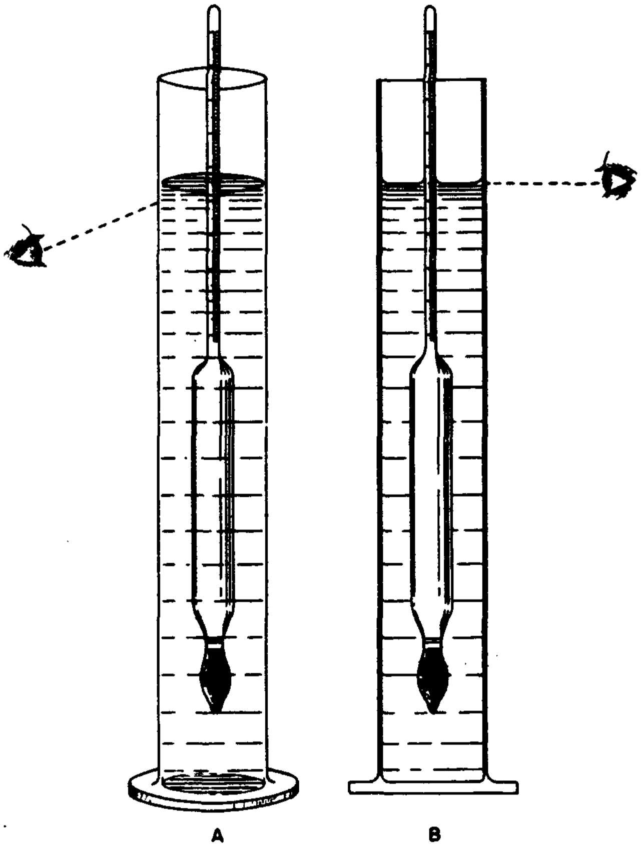

FIGURE 20. *Method of reading hydrometer (NBS Circular C410).*

the temperature at which the hydrometer is observed differs from the temperature at which the hydrometer was calibrated, the reading is not truly the density according to the basis of the hydrometer. The indicated reading differs from the normal reading by an amount depending on the difference in temperature and on the relative thermal expansion of the hydrometer and the liquid. Tables of corrections may be prepared for use with hydrometers at various temperatures. Such tables should be used with caution, and only for approximate results when the temperature differs much from the temperature at which the hydrometer was calibrated or from the temperature of the surrounding air.

Effects of surface tension on hydrometers are a consequence of the downward force exerted on the stem by the meniscus or curved surface, which rises about the stem, and affects the depth of immersion and consequent scale reading. Because a hydrometer will indicate differently in two liquids having the same density but different surface tensions, and since surface tension is a specific property of liquids, it is necessary to specify the liquid for which a hydrometer is intended. Although hydrometers of equivalent dimensions may be compared, without error, in a liquid differing in surface tension from the specified liquid, comparisons of dissimilar hydrometers in such a liquid must be corrected for the effect of the surface tension.

In many liquids spontaneous changes in surface tension occur due to the formation of surface films of impurities, which may come from the liquid, the vessel containing the liquid, or the air. Errors from this cause are avoided by the use of liquids not subject to such changes or by the purification of the surface by overflowing immediately before reading the hydrometer. The latter method is used at the National Bureau of Standards for testing hydrometers in sulfuric-acid solutions and alcohol solutions, and is accomplished by causing the liquid to overflow from the part of the apparatus in which the hydrometer is immersed by a small rotating propeller which serves also to stir the liquid. The apparatus is shown in figures 21 and 22.

A simpler but less precise apparatus designed to permit renewal of the surface of a liquid by overflowing, is shown in figure 23. The cylinder is filled nearly to the spout by the liquid, the density of which is desired or in which hydrometers are to be compared. The hydrometer is then immersed in the liquid and permitted to float freely until it has assumed the temperature of the liquid. The hydrometer is raised to permit thorough stirring of the liquid and the temperature is observed. From a beaker containing the liquid at the same temperature a sufficient amount is poured into the funnel to cause the liquid to overflow and run out the spout, where it is caught in a convenient vessel. The hydrometer is then read. The completeness of the cleansing of the surface of the liquid may be tested by repeating the operation. The readings of the hydrometer will approach a constant value as the surface becomes normal.

The necessity for such special manipulation is confined to the reading of hydrometers in liquids which are subject to surface contamination. Such, in general, are aqueous solutions or mixtures of acids, alkalies, salts, sugar, and weak alcoholic mixtures. Oils, alcoholic mixtures of strength above 40 percent by volume, and other liquids of relatively low surface tension are not, in general, liable to surface contamination sufficient to cause appreciable changes in hydrometer readings.

The accuracy of hydrometer readings depends, in many cases, upon the cleanness of the hydrometers and of the liquids in which the observations are made. In order that readings shall be uniform and reproducible, the surface of the hydrometers,

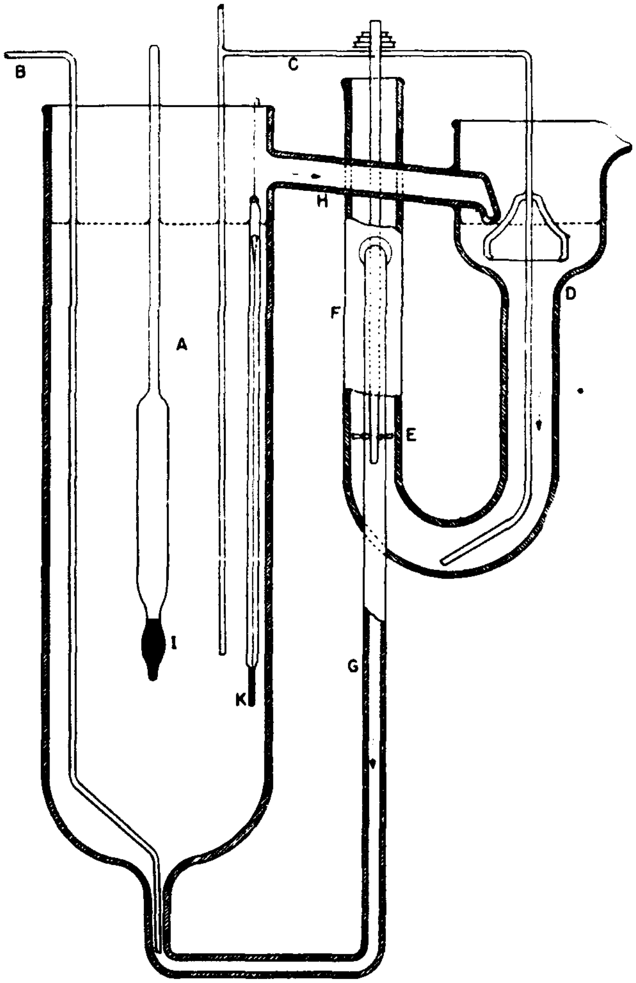

FIGURE 21. *Section of hydrometer comparator (Peffer and Blair, NBS Circular 477).*

A, Cylinder containing the test liquid; B, glass tube for filling and emptying A; C, siphon for removing the liquid from D into A; E, propeller that stirs the liquid and raises it in the tube F, making it flow through G into A and through the cross tube H, into D; I, hydrometer; K, thermometer.

and especially of the stem, must be clean, so that the liquid will rise uniformly and merge into an imperceptible film on the stem. The readiness with which this condition is fulfilled depends somewhat upon the character of the liquid. Certain liquids, such as mineral oils and strong alcoholic mixtures, adhere to the hydrometer stem very readily, while with weak aqueous solutions of sugar, salts, acids, and alcohol, scrupulous cleaning of the stem is required in order to secure the normal condition. Before use, the hydrometer should be thoroughly washed in soap and water, rinsed, and dried by wiping with a clean linen cloth. If the hydrometer is to be used in aqueous solutions which do not adhere readily, the stem should be dipped into strong alcohol and immediately wiped dry with a soft, clean, linen cloth.

A careful observer can, by using a hydrometer that has been accurately calibrated, obtain results that are correct to within one of the smallest subdivisions of the scale. For example, a "precision" hydrometer should yield densities that are accurate to one unit in the third decimal place, or, if graduated in percentages, to 0.1 percent. This degree of accuracy can be considerably improved by the exercise of special precautions as to temperature control, cleanliness, etc.

There are a number of arbitrary scales in use to represent the densities or specific gravities of liquids.

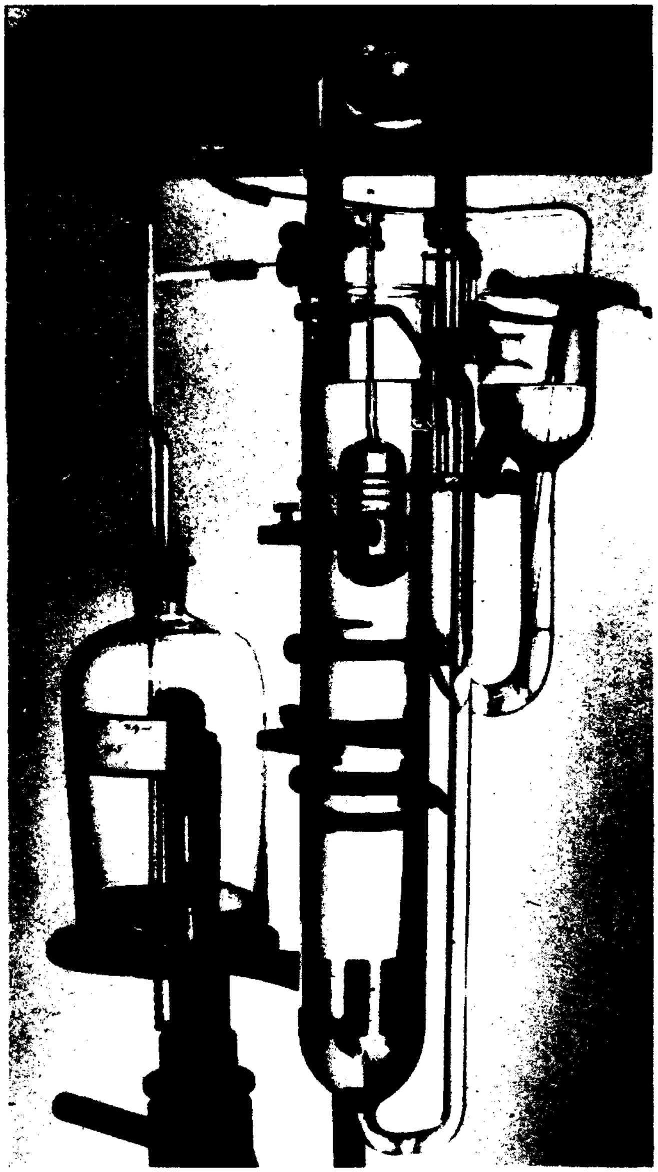

Figure 22. *Hydrometer comparator (Peffer and Blair, NBS Circular 477).*

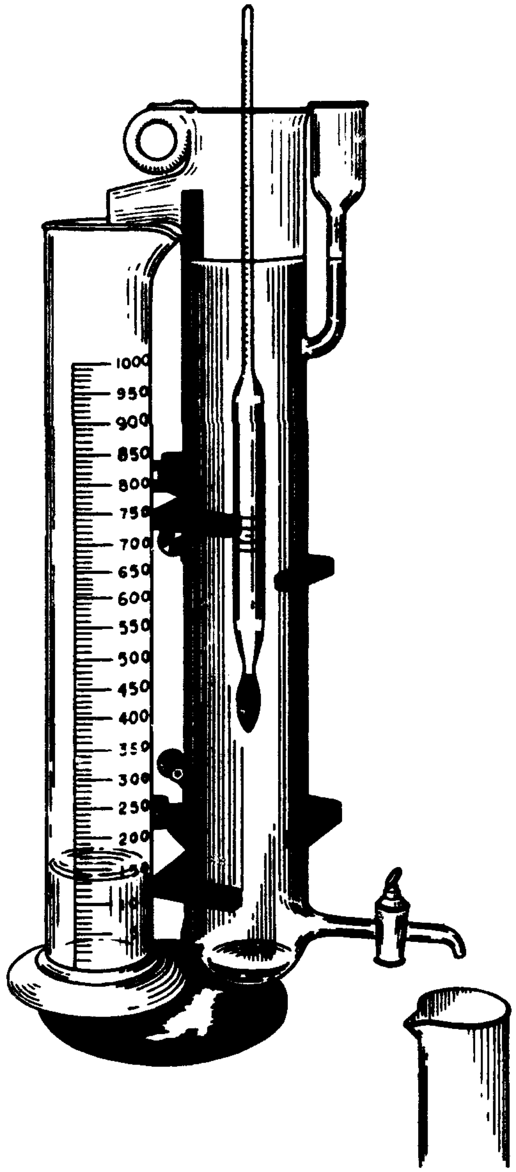

Figure 23. *Apparatus for renewal of surface by overflowing (NBS Circular 16).*

Two Baumé hydrometer scales are in general use in the United States. The following formula is used for liquids heavier than water:

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{sp gr } 60°/60° \text{ F}}. \quad (13)$$

For liquids lighter than water, the formula is

$$\text{Degrees Baumé} = \frac{140}{\text{sp gr } 60°/60° \text{ F}} - 130 \quad (14)$$

The modulus 141.5 instead of 140 in eq 14 was also used in the petroleum-oil industry. In order to overcome the confusion that existed in this industry by reason of the use of two so-called Baumé scales for light liquids, the American Petroleum Institute, the U. S. Bureau of Mines, and the National Bureau of Standards in December 1921 agreed to recommend that in the future only the scale based on the modulus 141.5 be used in the petroleum-oil industry, and that it be known as the API scale. The relation of degrees API to specific gravity is expressed by the formula

$$\text{Degrees API} = \frac{141.5}{\text{sp gr } 60°/60° \text{ F}} - 131.5 \quad (15)$$

The Baumé scale based on the modulus 140 continues to be in general use for other liquids lighter than water. Tables of specific gravities corresponding to degrees Baumé for both heavy and light liquids and to degrees API for petroleum oils, have been published [2, 52].

Hydrometers or lactometers for determining the specific gravities of milk are usually read in Quevenne degrees. The relation of Quevenne degrees to specific gravity is expressed by the formula

$$\text{Quevenne degrees} = 1000\ (\text{sp gr} - 1). \quad (16)$$

On account of the opaqueness of milk, it is customary practice of manufacturers to calibrate lactometers to be read at the top of the meniscus at 60° F.

The Bureau of Dairy Industry, United States Department of Agriculture [53] recommends the following procedure in preparing a sample of milk prior to a determination of its specific gravity. If the milk is freshly drawn or has been unduly shaken in transit or handling so that considerable air has been incorporated, it should be held at a temperature not lower than 50° F for 3 or 4 hours to allow trapped air to escape. Cool the sample of milk rapidly to a temperature between 35° and 40° F and hold it at this temperature 4 to 6 hours. Then allow the milk to warm up slowly during at least a half-hour period to 55° F. Mix the cream layer into the milk by pouring carefully back and forth several times, each time allowing the milk to run down the inside wall of the receptacle to avoid incorporating air. Taking the same care, pour the mixed milk into a cylinder which, with the lactometer, has been previously cooled in a water bath to 58° F. Immerse the cylinder in the water bath and bring the water bath and milk rapidly to a temperature of 60° F, taking care not to exceed that temperature. Before reading the mark on the lactometer stem at the top of the meniscus be sure that the lactometer floats freely and that the stem above the milk is clean and dry.

Plato, Domke, and Harting [54] derived the following relation between the specific gravity and the percentage of sucrose in sugar solutions:

$$\begin{aligned}\text{Sp gr } 15°/15°\text{C} = 1 + (&387.7655p + 1.33945p^2\\ &+ 0.0048303p^3 - 0.0000053546p^4 \qquad (17)\\ &- 0.00000008400p^5)10^{-5},\end{aligned}$$

where p is the percentage of sucrose from 2.5 to 76. A table of specific gravities corresponding to various percentages of sucrose by weight (Brix) from 0 to 95 and to Baumé (modulus 145) degrees from 0 to about 49.5, was published by Snyder and Hammond [55].

The barkometer, Twaddle (also spelled Twaddell), and Baumé hydrometer scales are in common industrial use in the leather-tanning industry for determinations of the specific gravities of tanning extracts. The following formulas give the relations between specific gravity and barkometer and Twaddle degrees, respectively:

$$\text{Degrees barkometer} = \frac{\text{Sp gr } 60°/60° \text{ F} - 1}{0.001}, \quad (18)$$

$$\text{Degrees Twaddle} = \frac{\text{Sp gr } 60°/60° \text{ F} - 1}{0.005}. \quad (19)$$

The relation between degrees Baumé and specific gravity is given by eq 13. Tables giving corrections to observed degrees barkometer, Twaddle, and Baumé, at various temperatures between 50° and 100° F in order to obtain corresponding degrees at 60° F, have been published by Blair and Peffer [56].

5. Falling-Drop Method

The falling-drop method for determining the density of liquids was developed by Barbour and Hamilton [57, 58]. This method consists in measuring the falling time of a small drop of liquid of known size through a definite distance in an immiscible liquid of known density. The latter liquid (reference liquid) should have a slightly lower density than the liquid drop. Using bromobenzene-xylene mixtures for the reference liquids, Barbour and Hamilton [59] obtained the densities of 0.01 ml of aqueous solutions to an accuracy of 0.0001. Vogt and Hamilton [60] refined this method by means of accurate temperature control and an improved pipette so that it is possible to determine the densities of 10-mm^3 (approx. 0.01 ml) samples to within 2.5 parts per million.

The density of a falling drop of liquid may be computed from eq 20 or 21 derived from Stokes' law.

$$D=D_0+\frac{18V\mu}{gd^2} \tag{20}$$

or

$$D=D_0+\frac{k}{t}, \tag{21}$$

where

D=density of drop of liquid
D_0=density of reference liquid
V=velocity of drop of liquid
μ=coefficient of viscosity of reference liquid
g=acceleration due to gravity
d=diameter of drop of liquid
k=a constant depending upon the viscosity of the reference liquid, the size of the falling drop of liquid, and the distance over which the drop is timed
t=time of fall of drop over a fixed distance.

Figure 24 shows the apparatus used by Hoiberg [61] for determining the specific gravity of petroleum oils by the falling-drop method. Three Pyrex-glass tubes with a 1.3-cm bore and 50 cm long, were marked with lines 30 cm apart, extending all the way around the tubes, one line being 5 cm from the end of the tube. Rubber stoppers were inserted to close the ends of the tubes nearest to the lines. The tubes were mounted in a 2-liter cylinder by means of a brass plate standing on three 1-cm legs and with a cap on the top. The three holes fitting the glass tube in the brass plate and cap were drilled with their centers on the apexes of an equilateral triangle and 3.5 cm apart. Holes were also drilled in the cap for a thermometer, a 250-watt knife-blade heater, and an expansion-type thermoswitch. Copper tubing 0.3 cm in diameter was run down the side of the cylinder to supply air for stirring the water bath. A leveling stand and leveling screws were provided. The thermometer was suspended so that it could also be used as a plumb bob to adjust the glass tubes in a vertical position.

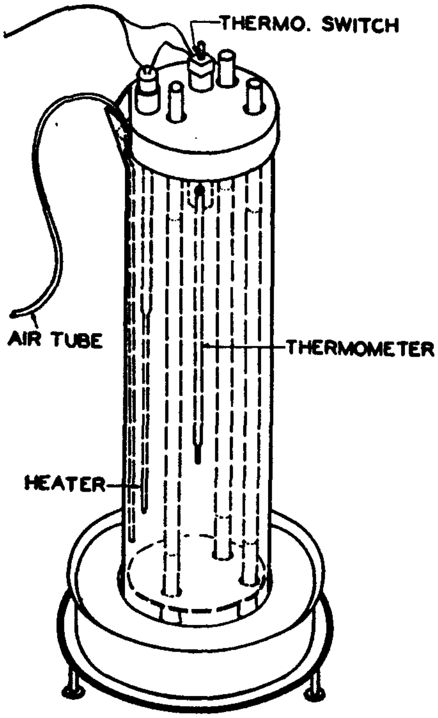

Figure 24. *Apparatus for determining the specific gravity of liquids by falling-drop method (Hoiberg).*

Solutions of ethyl alcohol and distilled water were mixed to cover the range in specific gravity of various petroleum oils. Before filling the glass tubes the solutions were heated to boiling under a reflex condenser to dispel air. The temperature of the solution in the glass tubes should be maintained constant.

A falling-drop pipette calibrated to deliver 2 drops of 0.01 ml volume each was used by Hoiberg to form the drop of petroleum oil, a pipette controller being used to regulate the delivery of the pipette. The time of fall of the drop was measured with an electric timer to within 0.1 second, and the specific gravity was obtained from a calibration curve.

Pipettes for obtaining drops of liquids of uniform size for determinations of density by the falling drop method have been described by Hochberg and LaMer [62] and Rosebury and van Heyningen [63].

Because bromobenzene and xylene mixtures are volatile, Frilette and Hanle [64] used solutions of phenanthrene in α-methylnaphthalene as reference liquids in measuring the specific gravity of water samples having D_2O contents ranging from 10 to 40 percent. Keston, Rittenberg, and Schoenheimer [65] used *o*-fluorotoluene as a reference liquid for determinations of density of water (with low contents of deuterium oxide). Frilette and Hanle state that *o*-fluorotoluene is not suitable for water that has a deuterium-oxide content much above 7 percent, for the precision of the falling-drop method falls off rapidly as the difference in density of the water and reference liquid increases.

Kagan [66] used a mixture of methyl salicylate and mineral oil as a reference liquid in determinations of the specific gravity of blood serum and plasma by the falling-drop method. Table 5 gives a comparison of the specific gravities of samples of serum and plasma by the falling-drop method and the picnometer method.

TABLE 5. *Comparison of specific gravities of samples of serum and plasma by the falling-drop method and the picnometer method (Kagan)*

Specific gravity		Difference
Falling-drop method	Picnometer (2 ml) method	
SERUM		
1.0285	1.0288	−0.0003
1.0256	1.0254	+.0002
1.0222	1.0222	.0000
1.0281	1.0283	−.0002
1.0283	1.0283	.0000
1.0306	1.0304	+.0002
1.0280	1.0280	.0000
1.0286	1.0290	−.0004
1.0280	1.0283	−.0003
1.0289	1.0292	−.0003
1.0303	1.0302	+.0001
1.0283	1.0279	+.0004
1.0209	1.0210	−.0001
1.0277	1.0279	−.0002
1.0285	1.0286	−.0001
1.0278	1.0274	+.0004
1.0297	1.0295	+.0002
1.0220	1.0220	.0000
1.0287	1.0284	+.0003
1.0261	1.0262	−.0001
OXALATED PLASMA		
1.0234	1.0233	+0.0001
1.0310	1.0312	−.0002
1.0268	1.0268	.0000
1.0330	1.0328	+.0002
1.0234	1.0232	+.0002
HEPARINIZED PLASMA		
1.0272	1.0274	−0.0002
1.0297	1.0298	−.0001
1.0221	1.0223	−.0002

Temperature changes in the reference liquid, variations in the size (diameter) of the falling drop, and errors in measurement of the time of fall of the drop, are important sources of error.

6. Balanced-Column Method

If one arm of a communicating U-tube contains a liquid having a density D_1 at any temperature and pressure, and the other arm contains an immiscible liquid having a density D_2 at the same temperature and pressure, then

$$\frac{D_1}{D_2}=\frac{h_2}{h_1}, \tag{22}$$

where h_1 is the height of the liquid in the first arm of the U-tube, and h_2 is the height of the liquid in the second arm (both heights are measured from the separating horizontal plane between the two liquids). If the density of one liquid is known, the density of the other liquid can be computed from eq 22.

Wiedbrauck [67] found that the densities of several liquids (ethyl alcohol, methyl alcohol, benzol, 10-percent solution of potassium hydroxide, and sulfuric acid) that he determined by the balanced-column method are accurate to 0.2 percent when compared with determinations by the hydrostatic weighing and picnometer methods. Frivold [68] claimed an accuracy of about 2×10^{-7} in his determinations of the differences of the density of water by this method.

An apparatus for simultaneous determinations of the densities of two or more liquids by the balanced-column method was described by Ciochina [69].

7. Method Based on Boyle's Law

Gallay and Tapp [70] applied Boyle's law to determine the density of leather by a simple method making use of the displacement of air. Their precision on a sample of about 2 g is approximately 0.3 percent. Thuau and Goldberger [71] and Edwards [72] also applied methods based on Boyle's law. The former gave no data. Edwards used a complicated procedure, which he admitted was in error by about 1.3 percent.

Kanagy and Wallace [73] determined the density of leather with an apparatus similar to that used by Gallay and Tapp. A diagram of the apparatus used by Kanagy and Wallace is shown in figure 25. A vessel, *A*, is connected at both ends with capillary tubing. The volume was calibrated between points *X* and *Y* on the capillaries and was found to be 10.734 ml. *B* is another vessel, which serves as the container for the sample and is connected to *A* with capillary tubing and the three-way stopcock, *F*. *A* and *B* have an

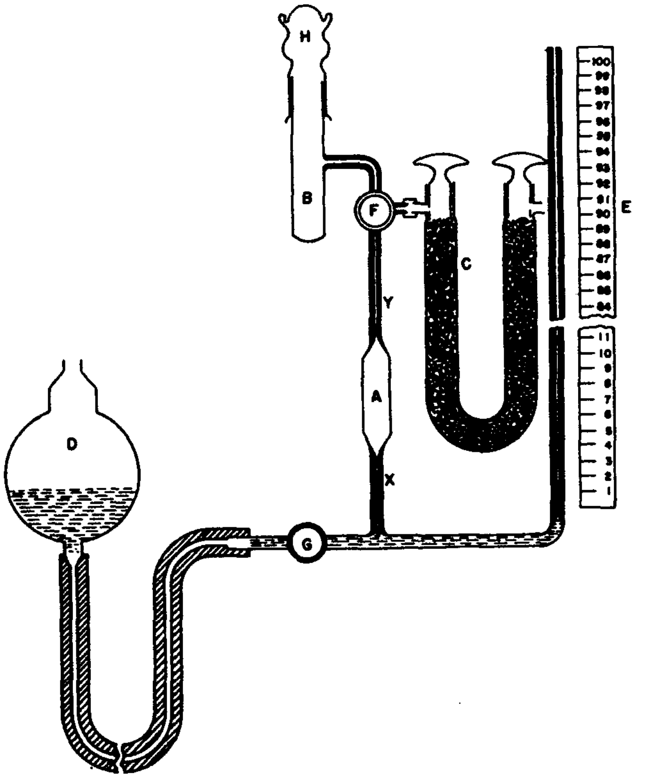

FIGURE 25. *Diagram of apparatus for density by method based on Boyle's law (Kanagy and Wallace).*

inlet through stopcock *F* and the U-tube, *C*, which contains anhydrous calcium sulfate to dry the air drawn into vessel *A* and to prevent the condensation of water vapor in *B* on compression. The volume of *B*, including the capillary arm to *Y*, is about 18 ml. Cap *H* fits over the outside of *B*, thereby eliminating the possibility of the leather coming into contact with the lubricating grease. The cap is fitted with glass lugs and held securely by means of wire springs. *D*, a cup containing mercury, is attached to the main apparatus with rubber tubing and is used to raise and lower the mercury level in A.

With stopcock *F* open to the U-tube *C* and the vessel *A*, the mercury level in *A* is raised to *Y* by lifting mercury cup *D*. Then dry air is drawn into *A* through *C* by lowering the mercury to *X*. *F* is closed to *C* and opened to *A* and *B*. The sum of the volumes of *A*, *B*, and the connecting capillaries may be represented by V_1, and the barometric pressure by P_1. The mercury level is then raised from *X* to *Y*, and stopcock *G* is closed. The volume of *B* and the capillary arm to *Y* may be represented by V_2, and the barometric pressure, *P*, plus the increase in pressure shown on manometer *E* caused by the compression (ΔP_1), by P_2. All values of pressure are read in centimeters of mercury. Then substituting in Boyle's law for a given mass of gas at a given temperature,

$$P_1V_1=P_2V_2 \tag{23}$$

$$P(A+B)=(P+\Delta P_1)B \tag{24}$$

or

$$B=\frac{PA}{\Delta P_1}. \tag{25}$$

The volume of *B* is calculated from eq 25. When a sample of leather having a volume *L* is placed in vessel *B* and the procedure repeated,

$$P(A+B-L)=(P+\Delta P_2)(B-L) \tag{26}$$

or

$$L=B-\frac{PA}{\Delta P_2}. \tag{27}$$

The density of the sample is then

$$D=\frac{M}{L}, \tag{28}$$

where *D* is the density, *M* is the mass of the sample, and *L* is the volume of the sample.

Kanagy and Wallace made density measurements on samples of leather weighing from 2 to 6 g. The samples were conditioned for at least 48 hours at 65±2 percent relative humidity and 70°±2° F, and all determinations were made in a room controlled at these conditions.

The precision of the determinations is influenced largely by two factors—pressure measurements and the size of the sample. On repeat measurements, the manometer readings varied about 0.5 mm. This variation is equivalent to 0.016 ml for a 2-g sample having a volume of 1.5 ml, or an error of approximately 1 percent. To test the apparatus, the volume of a piece of copper wire 100 cm in length and of uniform diameter was determined from dimensional measurements. Its volume was then determined by the apparatus. The volume by dimensional measurement was 1.319 cm^3 and as determined by the apparatus 1.303 ml. These values illustrate the precision of the method for volumes less than 2 ml. For a 6-g sample having a volume of about 4 ml, the error is equivalent to about 0.007 ml or less than 0.2 percent. The apparatus was again tested with a piece of brass tubing that had a larger volume than the copper wire. The volume calculated by dimensional measurements was 4.014 cm^3, whereas that determined with the apparatus was 4.010 ml. The difference is smaller than that calculated from the reproducibility of the readings, and illustrates the precision possible for samples having volumes greater than 2 ml. Unfortunately no comparison was made of densities by this method and by another density method, such as hydrostatic weighing or the use of a picnometer.

A reported value of the density of a sample of leather should be accompanied by a statement of the temperature and relative humidity at which it was determined.

8. Electromagnetic Method

Richards [74] constructed an apparatus for rapid determinations (about two hundred 5-ml samples of liquids every 8 hours) of the densities of small samples of liquids. Ordinary hydrometers and picnometers were unsuitable for his purpose, since the former require at least 20-ml samples, whereas the latter are too slow.

The essential parts of the apparatus consist of a small glass float held under the surface of the sample of liquid by an adjustable stop and a small coil surrounding the lower portion of the sample tube. If current passing through the coil is gradually increased, the resulting magnetic field will eventually exceed a critical value, such that the force on an armature (made from a short piece of an iron nail) will become sufficient to draw the float away from a stop. The density of the sample of liquid may be determined by measurement of the critical current, from the equation

$$D=kI^2+D_F, \tag{29}$$

where *D* is the density of the sample of liquid, *k* is a constant, *I* is the critical current, and D_F the density of float.

Richards used alternating current from a step-transformer in the field coil to prevent permanent magnetization of the armature and to minimize sticking of the float. The value of I in eq 29 is, in practice, the value obtained with an alternating-current milliammeter. The sensitivity of the apparatus is increased and the range decreased by increasing the size of the float, reducing the size of the armature, and reducing the number of turns in the field coil. Surface-tension effects are eliminated by the electromagnetic method because the float is submerged.

A diagram of the apparatus for determinations of the density of liquids by the electromagnetic method is shown in figure 26. The float, A, constructed of Pyrex glass, encloses the armature. The average density of the float is adjusted by adding or removing glass at the tip until it just floats in liquid, the density of which corresponds to the lowest value of the range required. The inside diameter of the float tube should be about 2 mm greater than that of the float to ensure a free passage. The float is centered on the bottom of the stop. The lower end of the float tube is sloped to allow drainage, and the drain tube allows 0.5-mm clearance around the tail of the float. A three-way stopcock is sealed on after the coil is mounted; the lower limb is used as a drain, and the side limb serves to admit air for drying the apparatus. The bearing for the adjustable stop is cemented in place after insertion of the float.

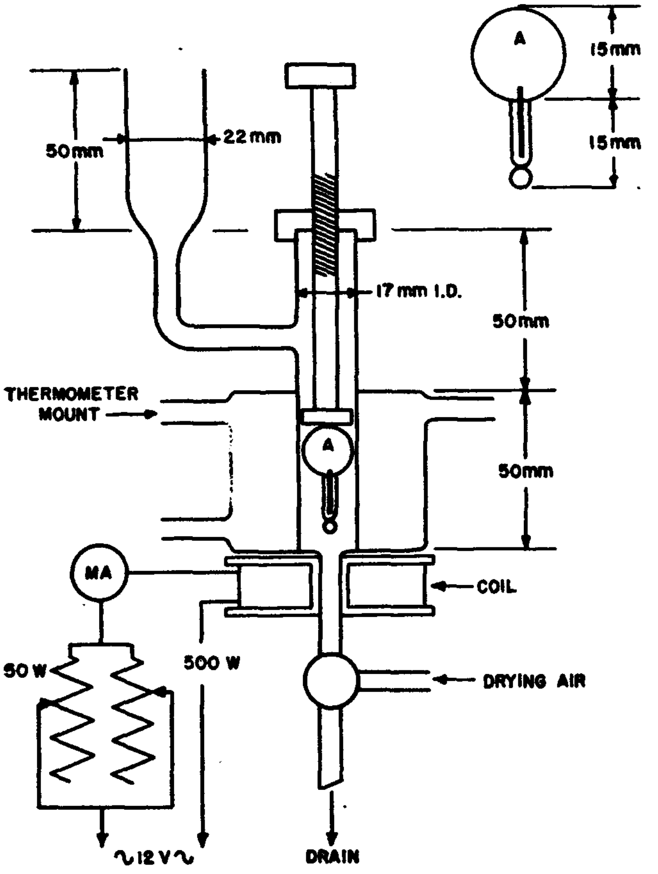

Figure 26. *Diagram of apparatus for determinations of the density of liquids by electromagnetic method (Richards).*

The coil is wound on an ebonite former with a thin core and consists of about 28 g of double cotton-covered copper wire No. 23 AWG. It is connected in series with a 20-volt alternating-current transformer and a variable-resistance assembly.

A water jacket surrounding the float chamber is used to maintain a constant temperature during determinations. Richards found it easy to maintain a temperature constant to within 0.2 deg C, which produces an error of less than 0.0002 g/ml in the densities of gasoline fractions.

A comparison of densities obtained by the electromagnetic and picnometer methods is given in table 6. The first column gives the critical currents used in the former method.

Table 6. *Comparison of densities obtained by electromagnetic and picnometer methods (Richards)*

Current	Density		Difference
	Electromagnetic method	Picnometer method	
amp			
0.085	0.626	0.6255	0.000
.152	.637	.6370	.000
.179	.643	.6429	.000
.223	.656	.6563	.000
.302	.684	.6842	.000
.383	.723	.7230	.000
.397	.732	.7309	+.001
.424	.746	.7445	+.002
.425	.747	.7458	+.001
.445	.759	.7598	−.001
.459	.768	.7673	+.001
.475	.778	.7795	−.002
.477	.780	.7811	.001
.488	.788	.7874	+.001
.500	.797	.7962	+.001
.502	.798	.7974	+.001
.515	.807	.8082	−.001
.521	.813	.8146	−.002

9. Elastic Helix Method

In the elastic helix method by Wagner, Bailey, and Eversole [75], a fused-quartz helix and a fused-quartz bob suspended in a homogeneous medium (liquid or gas) were used to determine the density of this medium. The helix and the bob are buoyed up according to Archimedes' principle, causing a change in the length of the helix. The length of the helix can be related to density by calibration in a series of media of known density.

The relative density of a medium can be calculated from the equation

$$D = D_S + \frac{a(T_S - T) - (L_S - L)}{b}, \qquad (30)$$

where L is the length of the helix in a medium of density D at a temperature T, L_S is the length of the helix in the standard medium of density D_S at the standard temperature T_S, and a and b are constants.

The absolute density of a medium can be computed from eq 31.

$$D=\frac{a(T_S-T)-(L_S-L)}{-\left(\frac{\partial L}{\partial M}\right)_T (V_b+V_h)}, \tag{31}$$

where L is the length of the helix in a medium of density D at a temperature T, L_S is the length of the helix in the standard medium of density D_S at the standard temperature T_S, V_b is the volume corresponding to the apparent effective mass of the bob, V_h is the volume corresponding to the apparent effective mass of the elastic helix, and $(\partial L/\partial M)_T$ can be determined from the changes in length of the helix caused by the addition of small weights to a platinum bucket suspended from the helix in a medium of constant density and temperature.

The elastic-helix method should be useful for measurements of densities in systems that are not accessible to measurements by other methods. Liquid or vapor densities can be determined accurately to the fourth significant figure by this method.

10. Ice Calorimeter Method

An ice calorimeter was used by Ginnings and Corruccini [76] for determining the density of ice at 0° C. In this device, the heat to be measured is allowed to melt ice that is in equilibrium with water in a closed system, and the resulting volume decrease is determined by means of mercury drawn into the system. The calibration factor, K, of this ice calorimeter (ratio of heat input to mass of mercury intake) is related to the heat of fusion, L, of ice, the specific volumes of ice, v_i, and water, v_w, and the density of mercury, d_m, by the equation

$$K=\frac{L}{(v_i-v_w)d_m}. \tag{32}$$

By using eq 32, the density of ice at 0° C and 1-atmosphere pressure may be calculated from the calibration factor of the ice calorimeter, the heat of fusion of ice, and the densities of water and mercury. Using 270.37 int. j/g of mercury for the calibration factor, 0.999868 g/ml for the density of water, 13.5955 g/ml for the density of mercury, and 333.5 int. j/g for the heat of fusion of ice, Ginnings and Corruccini calculated the density of ice to be 0.91671 g/ml at 0° C and 1-atmosphere pressure. The largest uncertainty in this calculation is believed to be caused by the uncertainty of 0.06 percent in the heat of fusion of ice, which is equivalent to 0.00005 g/ml in the density of ice.

Numerous measurements of the density of ice have been reviewed by Dorsey [77]. The results of these measurements have been so scattered that some observers have believed the density of ice to be not strictly constant. The value given in the International Critical Tables [78] for the density of ice at 0° C and 1-atmosphere pressure is 0.9168 ±0.0005 g/ml. Ginnings and Corruccini believe that the ice-calorimeter method provides the most accurate determination of the density of ice, since this method is free from many of the difficulties inherent in other methods. On account of the filaments and cracks that all samples of ice appear to have, any experimental method that measures the "bulk" density of ice will obviously give a different result from methods, such as the ice-calorimeter method, which determine the true density. No evidence has been obtained with the ice calorimeter that the true density of ice is anything but constant.

11. Volumetric Method

The approximate density of a solid having a definite geometrical form may be determined by a volumetric method. In this method the volume is computed from measurements of the dimensions of the solid. The weight of the solid is obtained in a convenient manner. The density of a solid determined by this method is probably accurate to about 1 percent.

Peffer [79] was unable to obtain accurate determinations of the density of artificial graphite by the hydrostatic weighing method, because this material absorbs liquids such as water, kerosine, toluol, etc. He therefore used the volumetric method for determinations of the densities of five samples of artificial graphite.

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WASHINGTON, June 15, 1949.

U. S. GOVERNMENT PRINTING OFFICE: 1950