Density of Liquid *n*-Octane

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A hydrostatic weighing apparatus is described for the measurement of liquid densities at ambient pressure with an absolute accuracy of ±1 × 10^{-5} g/ml relative to water at 3.98°C. Density data for normal-octane were determined from —27–122°C at roughly five-degree intervals at atmospheric pressure. The worst experimental precision is ±1 × 10^{-6} g/ml. The results are compared with the best previous data.

The normal alkanes have been the subject of a great deal of study (*6, 12*). Theoretical investigations generally require highly accurate density data. Although several sets of density data exist for *n*-octane, there is a significant disparity among them (*1, 5, 7, 8, 13–15, 17*). This work was undertaken to resolve the density of normal octane at atmospheric pressure, and to provide a test of a rapid means of measuring such liquid densities to high accuracy.

EQUIPMENT

A highly accurate means of measuring atmospheric pressure liquid densities has been developed utilizing the displacement technique. For the hydrostatic weighing method, the density, ρ_t, is calculated:

$$\rho_t = \frac{(W_A - W_L)}{V_t} \frac{g_c}{g} \qquad (1)$$

where $g = 980.0018$ cm/sec² (*11*). The difference between the vacuum corrected weight of the sinker in air, W_A, and the weight of the sinker while suspended in the liquid, W_L, is the weight of the liquid displaced. V_t is the volume of the sinker at temperature *t*. An error analysis based on Equation 1 predicted an absolute accuracy of ±0.00001 g/ml. From this analysis, the design of the apparatus was formed. The sinker used was 168.94617 ml with a mass of 193.94098 grams.

METHOD

The apparatus is shown in Figure 1: balance *A*, density sinker *B*, density chamber *C*, and temperature bath, *D*. At *E*, a Leeds and Northrup platinum resistance thermometer was used to measure temperature ±0.01°C absolute and ±0.001°C relative to the 1968 International Practical Temperature Scale. It was calibrated by the NBS and found to be satisfactory as a standard. Temperatures below ambient were obtained by using a Neslab bath cooler, *F*. The glass tubing arrangement at *G* encases the suspension chain, *H*, from the balance table to the opening of the density chamber. This eliminates the effect of air currents on the weighings.

Error analysis indicated that the balance and the temperature bath were the critical components for high accuracy. To meet the weighing requirements, a Saratorius Model 2662 single-pan balance having a capacity of 200 grams and an accuracy of ±0.1 mg was chosen. The temperature bath is a Hallikainen Model 1128C which, with care, can be used to control within ±0.001°C of the set point. The power supply for the bath controller is a Sola constant voltage transformer. The apparatus was housed in a specially designed constant temperature and humidity room. The room was maintained at 25°C nominal, with monitored fluctuations of 0.1°C at any given point, through the use of a proportional controller. The humidity was maintained at 30% relative humidity (RH), nominal with monitored fluctuations of 1% RH at any given point.

Figure 2 is a diagram of the density chamber, *C*, and the density sinker, *B*, of Figure 1. The density sinker and the density chamber are constructed of borosilicate glass. A top view of this diagram is circular. This diagram consists of three major parts: sinker *A*, outer container *B*, and insert *C*, which fits inside the container. The outer cylinder and insert are joined together by a 75-mm O-ring joint at *D* providing a vacuum tight seal. There are three, 5-mm connections to the insert. Tube *E* is used for filling the chamber. The open end is a 5-mm O-ring joint attached to an apparatus for filling and degassing the liquid sample before filling. At *F*, a gas trap is provided to stop any loss of sample from the main chamber by evaporation. Tube *G* encases the suspension wire, *O*, which is connected to the suspension chain, *H*, in Figure 1, from the balance. At *H*, in Figure 2, an expansion bulb is provided so that the liquid level will remain constant in the density chamber. The tube, *I*, allows liquid to flow into the reservoir, *J* as the liquid expands thermally. Tube *L* is provided to remove liquid from the reservoir, *J*. At *M*, a glass ridge is formed on the insert so that a Teflon band can be placed between the cylinder and insert to form a baffle.

Sinker *A* has a glass ring, *N*, on top so that the supension wire, *O*, can be attached to the sinker. The other end of the suspension wire is connected to a hook from the suspension chain. The suspension wire is 0.005-in. diameter wire composed of 76% Ni, 20% Cr and traces of Fe and Al. The sinker has a rounded bottom *P*, to prevent vacuum welding while the chamber is being filled. Attached to the top portion of the sinker is a tube *Q* filled with mercury to give the sinker added weight.

The apparatus was washed in hot chromic acid, triply distilled water, and then vacuum dried prior to filling with the liquid sample. The sample was degassed and the apparatus was filled in vacuo to eliminate the possibility of air bubbles' forming on the sinker or suspension wire. With filling completed, the apparatus was aligned so that neither suspension wire nor sinker touched the tube *G* or the chamber *C*.

The apparatus was placed in the temperature bath and thermal equilibrium was established at the lowest data point temperature. Temperature may be increased only, owing to the design of the apparatus. A constant liquid level is required to maintain exactly the same amount of suspension wire under the liquid for each weighing, as the submerged section of the wire is included in the sinker volume due to the calibra-

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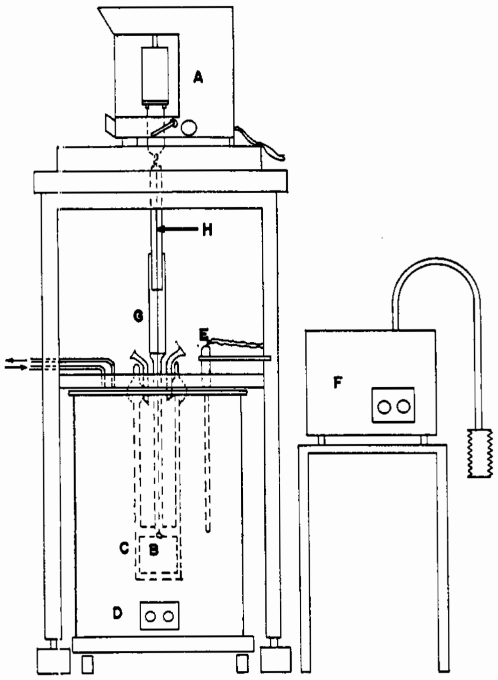

Figure 1. Density Apparatus

A.	Balance	E.	Platinum resistance thermometer
B.	Sinker	F.	Bath cooler
C.	Density chamber	G.	Glass tube
D.	Temperature bath	H.	Suspension chain

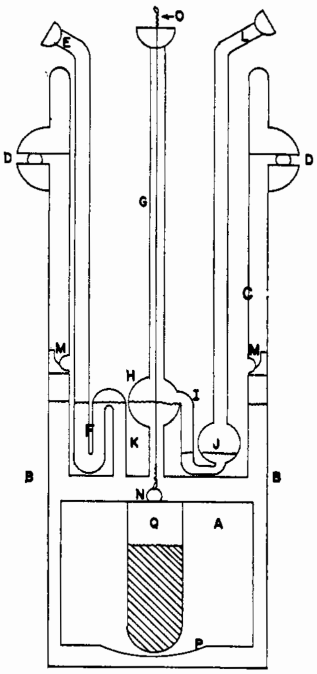

Figure 2. Density Chamber Detail

A.	Sinker	J.	Overflow reservoir
B.	Outer container	K.	Lead tube
C.	Insert	L.	Liquid withdraw tube
D.	O-ring joint	M.	Glass ridge and Teflon band
E.	Filling tube	N.	Sinker suspension ring
F.	Gas trap	O.	Suspension wire
G.	Tube	P.	Rounded bottom
H.	Expansion bulb	Q.	Mercury tube
I.	Overflow		

tion procedure. As temperature increases, liquid flows out of the chamber.

Several weighings at the selected temperature are taken to ensure consistency in the data being taken. After a set of weighings are recorded, a new temperature is selected and the procedure is repeated. This routine is repeated until the temperature is within 5°C of the boiling point of the liquid. This same technique was successfully used by Forziati (*7*) for many liquids. He also reported that the effect of any air dissolved at the surface was negligible.

When the bath temperature exceeded ambient, a heat lamp was used to keep the suspension chain free of condensing vapor. A stream of Argon was also passed over the wire to maintain a uniform gas density so that the buoyancy of the chain could be computed.

Research grade *n*-octane (99.92 mol % purity) was supplied by Phillips Petroleum Co. No treatment other than degassing was performed. The refractive index of the *n*-octane was 1.39512 at 25.00°C. This value falls within the range given in Timmerman's (*14*) for sodium light at 25.00°C. The research grade *n*-octane was also tested via gas-liquid chromatography. The ratio of the *n*-octane peak area to impurity peak area was on the order of 10000 to 1. The impurity peak area ratio between research grade *n*-octane and pure grade *n*-octane (99. mol % purity) was about 0.01. This implies that 99.92% is a conservative estimate of the purity of the octane used.

CALIBRATION

A calibration relative to water at 3.98°C was made to determine the volume of the sinker. The density of water was taken as 1.000000 g/ml at 3.98°C. The water used was taken from the Pacific Ocean near San Francisco Calif. Ocean water was used to assure a known isotopic ratio of D/H and O^{18}/O^{16} (*4*). About 2 liters of this water was distilled four times in a batch distillation. During the second distillation, the water was treated with NaOH and $KMnO_4$. From the initial amount of water used, 95.0% was retained to keep the initial isotopic ratios. The sample used was degassed prior to filling. The refractive index of the water was 1.33248 at a wavelength of 5892.Å (sodium light) at 25.00°C. This value is within experimental reproducibility of a value interpolated from index of refraction vs. temperature for water using sodium light (*16*).

To validate the apparatus, additional data were taken for water from 2–85°C. These data were then compared with water densities calculated from the rational function which Kell (*9*) has fit to existing high-accuracy water data. The comparison is well within experimental error in all cases and is reported in Figure 3. The apparent trend in the curve is probably due to the fact that Kell used the 1948 temperature scale while the 1968 scale is used here.

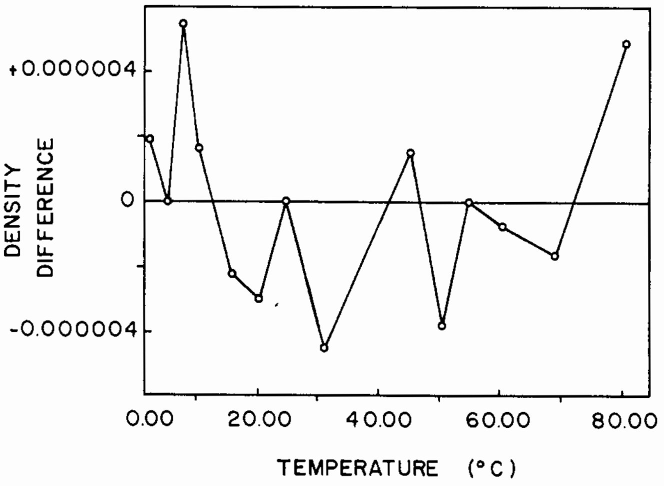

Figure 3. Comparsion of this study water data with literature water data

DATA REDUCTION

The basic measurement in the hydrostatic weighing technique is the weight of the sinker in the liquid at the desired temperature. This weight plus the sinker volume and sinker weight in vacuum, both of which are determined during the calibration phase, allow the calculation of the liquid density. The volume of the sinker, V_t, is calculated from:

$$V_t = V_c[1 + \alpha(t - 3.98)] \qquad (2)$$

The volume at 3.98°C, V_c, is obtained from the calibration. The coefficient of volume expansion, α, of the borosilicate glass sinker was found to be 0.997×10^{-5} as the value which gave the best fit of the water density calibration to Kell's (*9*) data. However, 0.997×10^{-5} is well within the limits for borosilicate glass (*10*). An error of 20% in α would be necessary to cause a recognizable (1×10^{-5} g/cc) error in density. The measured weight of the sinker is corrected for the surface tension force exerted by the liquid on the suspension wire (*1*). The densities are also corrected for the depth of immersion of the sinker using available values for the isothermal compressibility (*2*, *3*) of the liquid. The effect of compression of the sinker due to immersion was negligible.

RESULTS

The volume of the sinker was 168.94617 ml at 3.98°C. The comparison with existing high-accuracy water data is reported in Figure 3. The actual water data are not reported as they are slightly less accurate than existing water data.

The 1-atm *n*-octane densities determined in this study are reported in Table I. All densities reported in Table I are the average of at least three determinations made in succession. The third column reports the deviation of the points from the average.

A comparison was made of interpolated *n*-octane data of this study and existing data sources. It has been deposited with the ACS Primary Publications Microfilm Depository Service (Table II). The data were interpolated via a seven-point Lagrangian interpolation. In all cases, where reliable absolute error estimates were reported, the agreement is within experimental error in the literature data. It should be noted that almost all of the literature data are for air-saturated *n*-octane. Since the literature data are in general one order of magnitude and, in a few cases, two orders less accurate than the data of this study, the comparison is of little value except to determine which authors report absolute errors and which authors report precision for absolute error. This fact can be of great value when using other data by the same author.

The interpolation procedure did not reproduce the present data within experimental accuracy and thus is not recommended for that purpose.

Table I. Density of *n*-Octane

Temp, °C	Density, g/ml	Dev × 10^6, g/ml
−27.631	0.740343	1
−27.391	0.740248	0
−23.559	0.737247	0
−18.254	0.733167	0
−13.159	0.729164	0
−8.032	0.725127	0
−2.883	0.721054	0
1.314	0.717741	0
5.522	0.714387	0
9.994	0.710824	0
15.720	0.706241	0
26.103	0.697876	0
30.447	0.694350	0
35.570	0.690164	0
40.484	0.686141	0
44.909	0.682485	0
50.156	0.678145	0
54.909	0.674170	0
59.968	0.669939	1
64.782	0.665496	0
69.631	0.661722	0
74.512	0.657545	1
79.697	0.653064	1
85.472	0.648017	0
91.025	0.643120	1
95.769	0.638894	0
100.830	0.634384	1
106.208	0.629690	1
112.737	0.623899	0
117.367	0.619628	0
122.575	0.614554	0

NOMENCLATURE

t = temperature, °C
W_A = weight of sinker in air (corrected to vacuum), grams
W_L = weight of sinker in liquids, grams
V_t = volume of sinker at temp t, ml
V_c = volume of sinker at 3.98°C, ml
α = volume coefficient of thermal expansion for borosilicate glass, ml/°C
ρ_t = liquid density at temp t, g/ml

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