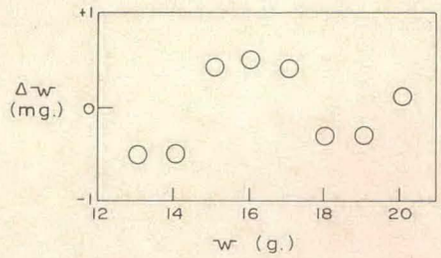

FIG. 3. The difference between the weights obtained using the balance and their nominal values (Δw) is plotted here as a function of the weight. The weights were calculated from the measured voltages with the aid of Eq. (1) and are compared with the calibrated values for a set of analytical weights. For this particular run, the average deviation is $\pm\frac{1}{2}$ mg over the 7 g variation in weight.

balance gas to the high pressure gas handling system was soldered to this section of the case. By minimizing the clearance between the balance itself and the cavity in the balance case, and by using small bore tubing throughout, the gas space volume of the entire system was held to 30 cc exclusive of the annular volume which was ordinarily filled with liquid.

Pressure measurements were made on an oil-filled dead weight gauge (Mansfield and Green) accurate to ± 0.007 kg/cm^2 or 0.01% up to 70 kg/cm^2 which was connected to the gas-filled system via a mercury U tube. A separate mercury manometer was available for measurements at or below atmospheric pressure. The pressure over the liquid in the cavity could readily be raised over the saturated vapor pressure without the addition of a foreign gas merely by condensing liquid into the inlet tube (6). Since this tube was in a fairly steep temperature gradient outside of the shield system, the temperature and vapor pressure of the liquid in the tube increased rapidly as the liquid level in the tube went up. No difficulties were encountered in putting the liquid in the cavity under pressures 50 atm in excess of the bulk vapor pressure. Heat conduction down the tube was negligible, and pressure and temperature equilibria were established too rapidly to measure after these pressure changes.

III. CALIBRATION AND PERFORMANCE

In order to calibrate the balance the Dewar can, shield, lower half of the copper block, and the magnesium sphere were removed. Analytical weights were then hung from the wire, and the coil currents required to null the beam were measured. The optical system for determining the beam position was such that the null position of the coil relative to the bar magnet could be reproduced to ~ 0.02 mm. It was found that the counterweight was such that the beam balanced with no current at a load of 16.2 g. Because of the arrangement of the magnet and coil, any changes in load were compensated by the electromagnetic force when the beam position was nulled. Therefore, this balance operated as a constant load, constant sensitivity device in which effects such as beam bending did not enter. The electrical connections to the coil could be reversed so that weights greater than or less than 16.2 g could be determined. It was found that the coil current was a precisely linear function of the weight, and that differences of 0.3 mg in load could be observed. If the voltage drop across the standard resistor in the coil circuit is denoted by E, a typical calibration run could be represented by

$$E=(w-16.1916)/15.188\,. \tag{1}$$

As an illustration of the quality of this balance, the differences between the weights calculated from Eq. (1) and the actual weights is plotted in Fig. 3 as a function of the weight. It appears that the accuracy and reproducibility of this balance is ~ 1 mg.

The volume of the magnesium ball was found to be 11.404 cc at room temperature, and the temperature dependence of the volume was obtained from the measurements of Hidnert and Sweeny[9] on the linear expansion of magnesium. If the changes in weight of this sphere can be measured to ± 1 mg, it thus appears that one can determine fluid density of 1 part in 10^4 if the density is ~ 1 g/cc, with a correspondingly lower accuracy at lower values.

Other than the temperature correction for the volume of the sphere, the only important correction to be applied is that for the buoyancy effects on the balance beam when operating with appreciable pressures in the balance case. If the change in weight due to the presence of liquid or gas in the balance is denoted by Δw, one has

$$\Delta w_t=\Delta w_{\text{ball}}+\Delta w_{\text{beam}}\,, \tag{2}$$

where the subscripts t, ball, and beam denote total weight change and weight change due to buoyancy of the ball and beam, respectively. Since the beam is immersed in gas at room temperature and a known pressure, one can write

$$\Delta w_{\text{beam}}=\rho_{\text{gas}}V_{\text{eff}}\,, \tag{3}$$

where V_{eff} is the effective volume of the beam and is a measure of the difference in the volumes of the two ends of the beam plus counterweight and coil; ρ_{gas} is the density of the gas, which is calculated from the equation of state of the substance at room temperature. V_{eff} was measured by determining Δw_t with the ball and cavity also at room temperature. In this case,

$$\Delta w_{\text{ball}}=\rho_{\text{gas}}V_{\text{ball}}\,. \tag{4}$$

The total weight change is equal to 15.188 ΔE, where ΔE is the difference between voltage drops for the balance with the system evacuated and filled with gas. In this way, the only unknown is V_{eff}. Results obtained when this quantity was determined using methane gas at room temperature are shown in Table I; the densities of the methane were

[9] P. Hidnert and W. T. Sweeney, J. Res. Natl Bur. Std. 1, 771 (1928).

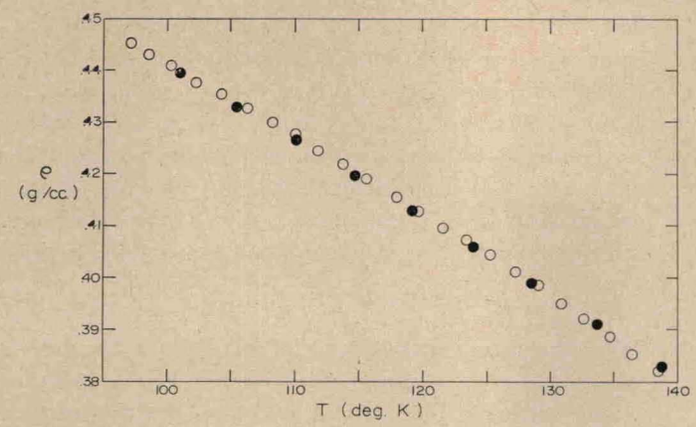

FIG. 4. Values of the density of samples of impure methane along the liquid-vapor equilibrium line are plotted here. The open circles were measured in this work, and the filled circles are obtained from the data of Keyes, Taylor, and Smith (see Ref. 11).

calculated from the equation of state data of Douslin, Harrison, Moore, and McCullough.[10] Note that the precision of the measurements is 3 parts in 10^3, which is to be expected for densities of $\sim 1/30$ g/cc. In this way, V_{eff} was found to be -1.13 cc; that is, the buoyancy of the arm with the counterweight is slightly larger than that of the arm with the coil.

IV. RESULTS

In Fig. 4, the measured densities of a sample of methane containing 0.4% nitrogen are compared with the data of Keyes, Taylor, and Smith,[11] who also used methane containing a small amount of nitrogen as impurity. In our experiments, the methane was condensed into the annulus around the sphere at a temperature slightly above the freezing point (90.6°K); a small excess pressure of $\sim\frac{1}{2}$ atm was maintained in order to ensure that the liquid level was well above the top of the magnesium sphere, and the currents required to balance the beam were recorded. It was found that the temperature of the block could be held constant to within 0.01°C for times up to $\frac{1}{2}$ h with no difficulty. The shields and block were both heated to raise the temperature above bath temperature (78°K) but when the heater on the block was turned off, its temperature became essentially constant after 5 min and remained so during the measurement, which typically required 10 min to determine coil current, temperature, and pressure. It is evident that our data are in excellent agreement with the literature results, at least for the impure samples. However, later experiments on more highly purified samples indicate that the densities of pure methane are slightly lower than those shown in Fig. 4, in agreement with other recent data.[12,13] The densities and isothermal compressibilites of pure methane and deuteromethane will be reported in detail elsewhere.

TABLE I. Buoyancy data using methane under pressure at room temperature.

P psia	ρ_{gas} g/cc	ΔE V	$V_{\text{eff}}+V_{\text{ball}}$ cc
276.6	0.01315	0.00887	10.24
370.0	0.01816	0.01230	10.29
398.8	0.01955	0.01327	10.31
476.3	0.02313	0.01569	10.30
501.5	0.02470	0.01662	10.22
576.6	0.02865	0.01938	10.27
588.2	0.02920	0.01970	10.25
678.8	0.03405	0.02297	10.25
710.8	0.04120	0.02414	10.28
807.8	0.04103	0.02767	10.24
812.6	0.04120	0.02808	10.35
		av	10.27±0.03 cc

ACKNOWLEDGMENT

The authors thank Professor G. Fleming of Pennsylvania State University for his invaluable assistance in the design and fabrication of the density balance.

[10] D. R. Douslin, R. H. Harrison, R. T. Moore, and J. P. McCullough, J. Chem. Eng. Data **9**, 358 (1964).
[11] F. G. Keyes, R. S. Taylor, and L. B. Smith, J. Math. Phys. **1**, 211 (1922).
[12] S. Fuchs, J. C. Legros, and A. Bellemans, Physica **31**, 606 (1965).
[13] A. J. Davenport, J. S. Rowlinson, and G. Saville (private communication).