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By observing the temperatures at which glass bodies were just equal in density to the liquid, the density of liquid UF_6 was measured along the saturation curve from the triple point (64.052°C) to 162.59°C. The density of the liquid at the triple point was found to be 3.630 g cm⁻³. Results of an earlier investigation are also reported. They confirm the later data, and lead to a value of 4.87 g cm⁻³ for the density of the solid at 62.5°C.

THE data presented in this paper were obtained during 1942 and 1943 in two separate investigations in the Low Temperature Laboratory of the National Bureau of Standards. The two investigations have been described in reports A-456 and A-1591 to the OSRD.

EXPERIMENTAL

Two different experimental methods were employed. In the first and less accurate investigation, the UF_6 was contained in a straight vertical tube in which the length of the column of liquid could be observed as a function of temperature. The material in the tube could also be frozen, and thus the relative densities near the triple point were obtained. The second and more accurate investigation dealt only with the liquid. In this investigation the liquid UF_6 was contained in a larger vertical glass tube which also contained six glass bodies (bobbins); see Fig. 1. The figure shows this tube connected to the supply cylinder ready for transfer of UF_6 into or out of it.

Measurements employing the second method were made after disconnecting the bobbin tube (Fig. 1) just beyond the first valve and placing it in a stirred liquid bath whose temperature could be accurately adjusted and controlled. This bath was contained in an unsilvered Dewar flask. Its temperature was determined with a platinum resistance thermometer whose coil was shielded from light by aluminum foil wrapped around the glass thermometer case.* By slowly raising the temperature and thus gradually reducing the density of the UF_6, the lowest bobbin was made to sink. Then the temperature was gradually lowered until the bobbin rose again. This cycle was repeated several times; then the temperature was raised until measurements could be made on the bobbin just above, and so on until all the bobbins had been measured. The bobbins were cut from glasses furnished us by the Glass Section of this Bureau, and were in the form of cylinders (length: 13 mm, diameter: 9.5 mm). One glass was specially prepared for us by

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J. C. Young and R. L. Brownell. Densities of the bobbins, as determined by the Density Section of this Bureau, are given in Table I. This table also contains cubical expansion coefficients furnished us by the Glass Section. Bobbin densities were measured before the bobbins were used and were remeasured between runs 1 and 2. The largest discrepancy in the two sets of measurements was only 1 part in 2900.

The bobbin tube was rather heavy, as the vapor pressure of the material at the highest temperature reached was estimated to be almost 13 atm. At the top the tube joined to a small U-tube containing KF as a getter, which in turn was attached through a copper-to-glass seal to a Teflon-packed brass valve with a stainless steel needle. This assembly was pressure-tested to 25 atmos. (abs.) at 190°C and as an additional precaution a ¾-inch glass plate was placed in front of the apparatus during measurements. The KF getter was activated by heating in vacuum at 300°C, and the supply cylinder was purged of all material volatile at dry ice temperature. Then connections were made as in Fig. 1 and sufficient liquid distilled into the tube to float all the bobbins with the lowest 3 or 4 cm above the bottom of the tube. The U-tube at T jacketed the transfer line. By drawing bath liquid through it occasionally the line was kept above the temperature at which UF_6 solidifies (64.052°C).

The apparatus used in the first investigation also employed a stirred bath contained in an unsilvered Dewar flask, but the bath occupied only the lower half of the flask. The air in the upper half could be warmed by a separate heater. Then when the UF_6 was to be frozen, the air space was kept slightly above the triple point and the water bath from 5 to 10 degrees below the triple point. The sample tube had an inside diameter of approximately 3 mm and a length of 123 mm. The material, when liquid, occupied about 80 mm of the tube. It was frozen by lowering it slowly from the hot air space into the cooler water bath. Successful freezing, without the trapping of gas bubbles in the solid, took from 4 to 5 hours. Measurements of the expansivity of the liquid were made in this apparatus

TABLE I. Densities and cubical expansion coefficients (β) of the glass bobbins.

Bobbin No.	Density at 23°C g cm^{-3}	β deg.$^{-1}$
6	3.608	27×10^{-6}
5	3.582	32
4	3.459	28
3	3.325	29
2	3.192	27
1	2.932	29

with the sample tube entirely submerged in the water bath. The length occupied by liquid was determined with a traveling microscope, by measuring the position of the meniscus relative to a fiducial scratch on the sample tube.

RESULTS

The density values obtained with the apparatus employing glass bobbins are given in Table II. The observed densities are those of the bobbins as given in Table I but corrected for thermal expansion from the temperature of calibration (23°C) to the temperatures of the various observations. Effect of pressure on the density of the bobbins was negligible, a reasonable value of the compressibility of glass (25×10^{-7} (kg cm^{-2})$^{-1}$) indicating an increase of only 3 parts in 100,000 at the highest pressure encountered. Each temperature of sinking is the lowest of several values obtained while slowly and steadily raising the temperatures of the bath, and conversely for each temperature of rising. There was no overlapping of sinking temperatures with rising temperatures. In run 1, bobbins 5 and 6 became wedged in the bottom of the sample tube and so could not be measured. Bobbin 1 was not measured because the pressure would have been too high for the sample tube. Hence after run 1 the material was removed, the tube broken and the bobbins quickly washed to prevent etching. The second run was then made using the same bobbins in a new tube (13 mm i.d., 20 mm o.d.). The densities obtained in the second run were consistently lower than those obtained in the first run by a little less than 1 per mille. There is no obvious explanation for the difference. If it is associated with the purity of the material, the first run is probably better, as the exhaustion of decomposition products from the supply cylinder prior to the second filling may not have been complete. However, because the second run covered the entire range and the first did not, the second run was used exclusively in deriving the equation representing the density.

The equation

$$\rho = 3.630 - 5.805 \times 10^{-3}(t - t_f) - 1.36 \times 10^{-5}(t - t_f)^2$$

with $t_f = 64.052$°C, represents the density of saturated liquid UF$_6$ within the experimental error

over the range covered by the measurements. The value of t_f, the triple point temperature, was taken from the work of Brickwedde, Hoge, and Scott.[1] Deviations from this equation are given in the last column of the table. At temperatures above the range of the data the equation gives densities that are too high. Considering all the likely sources of error, it seems reasonable to expect densities calculated from the equation to be correct within 3 per mille. About a third of this uncertainty may be attributed to the measurements and the rest to possible impurity of the material. The amount of impurity is difficult to estimate. The method of handling the material was similar to that used in reference 1 where the freezing-point curve indicated 2×10^{-4} as the mole fraction of impurity. The starting material in the present work was contained in a metal cylinder rather than in glass as in the other experiment, and the distilled liquid was distinctly orange-yellow although not opaque. This would indicate the presence of some molecular complexes of the form $(KF)_x(HF)_y(UF_6)_z$. A more serious possible impurity is SiF$_4$, which might be expected to have a partial molal volume considerably different from that of UF$_6$. The 2 per mille allowance, however, would cover an impurity 10 times as large as that observed in reference 1, even with a 2 to 1 ratio of partial molal volumes.

Data obtained on liquid UF$_6$ in the first and less accurate investigation are given in Table III. This investigation gave values of V/V_f, the ratio of the volume V at any temperature to the volume V_f of the liquid at the triple point. These data were corrected for the change in the mass of vapor above the liquid, but not for thermal expansion of the glass tube. The latter correction would have affected the observed densities by only 1 part in 3000 in the worst case, which is much less than the experimental errors. Since $V/V_f = \rho_f/\rho$ we may take the value of ρ_f (liquid) from the equation above (3.630 g cm^{-3}) and obtain densities corresponding to the data in Table III. We may also
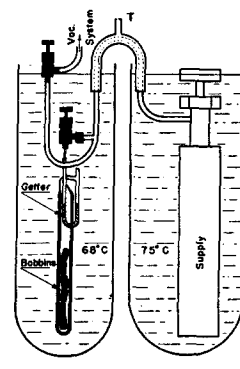

FIG. 1. Apparatus for transferring UF$_6$ into the experimental tube containing the bobbins. The tube was placed in a stirred liquid bath for the measurements.

[1] Ferdinand G. Brickwedde, Harold J. Hoge, and Russell B. Scott, "The low temperature heat capacities, enthalpies, and entropies of UF$_4$ and UF$_6$," J. Chem. Phys. 16, 429–36 (1948).

TABLE II. Densities of saturated liquid UF$_6$.*

Bobbin No.	Sinks °C	Rises °C	Av. °C	Obs. Density g cm^{-3}	Obs.-Calc. Density g cm^{-3}
		Run 1			
4	93.01	92.99	93.00	3.452	0.001
3	112.96	112.93	112.94	3.316	.002
2	131.48	131.44	131.46	3.183	.006
		Run 2			
6	68.69	68.63	68.66	3.604	.001
5	72.93	72.89	72.91	3.576	−.002
4	92.66	92.63	92.65	3.452	−.001
3	112.68	112.66	112.67	3.316	.000
2	131.17	131.07	131.12	3.183	.004
1	162.67	162.50	162.59	2.920	−.006

* Temperatures are those at which densities of UF$_6$ and glass bobbins became equal. Observed densities are those of the glass bobbins corrected for thermal expansion to the appropriate temperature. Calculated densities are from the equation.

calculate densities from the equation alone. "Observed" and calculated results obtained in this way (Table III, columns 3 and 4) necessarily agree at $t=t_f$, but the fact that the agreement is good throughout the range of the earlier measurements helps to corroborate both sets of data. Table III contains one value of V/V_f for the solid, at 62.5°C, which is 1.6° below the triple point. This is the most reliable of the values obtained by the process of slow freezing. Using the subsequently found value of ρ_f (liquid) the density of the solid at 62.5°C is found to be 4.87 g cm^{-3}. This value is probably correct within 5 per mille.

DISCUSSION

The density of liquid UF$_6$ had been measured previously by Homer F. Priest (OSRD Report A-139). His value of 3.667 g cm^{-3} at 65.1°C is higher than the value of 3.624 computed from our equation but the difference is less than his estimated error of ±0.05 g cm^{-3}. Ruff and Heinzelmann[2] found the density of solid UF$_6$ at 20.7°C to be 4.68, by a method involving displacement of CS$_2$.

The use of glass bobbins to determine density

[2] Otto Ruff and Alfred Heinzelmann, "On UF$_6$," Zeits. f. anorg. allgem. Chemie 72, 63–84 (1911).

TABLE III. Values of V/V_f obtained for saturated liquid UF$_6$ in the first investigation.*

t °C	V/V_f	Obs. Density g cm^{-3}	Obs.-Calc. Density g cm^{-3}
	Liquid, Run A		
62.45	0.997	3.641	0.002
71.31	1.013	3.583	−0.004
73.64	1.017	3.569	−0.004
73.64	1.017	3.569	−0.004
75.98	1.022	3.552	−0.007
83.00	1.034	3.511	−0.004
85.34	1.038	3.497	−0.003
90.03	1.048	3.464	−0.006
92.38	1.053	3.447	−0.008
	Liquid, Run B		
62.45	0.997	3.641	0.002
64.03	1.000	3.630	0.000
64.97	1.001	3.626	0.001
73.64	1.016	3.573	0.000
83.00	1.033	3.514	−0.001
92.38	1.051	3.454	−0.001
	Solid		
62.5	0.745	4.87	

* Observed densities are obtained from V/V_f by using ρ_f(liquid) =3.630 from the results of the second investigation. Calculated densities are from the equation.

was particularly convenient in the present experiments because the density of the liquid permitted solid bobbins to be used. With liquids of lower density the bobbins would have to be hollow. If calibrated glass bobbins were to become readily available the method might find much wider application than has been the case up to now.

In connection with the slow freezing of the material it was found that the lower end of the sample tube could be cooled nearly 7° below the triple point before freezing started. It was also found possible to keep the entire tube 1.6° below the triple point for periods of several hours without freezing of the liquid. We had been cautioned to expect abnormal breakage in glass tubes inside which UF$_6$ was permitted to solidify. In the second investigation solidification was not permitted. In the first, we were relieved to find that the sample could be taken from room temperature to the triple point in the space of a few minutes without breaking the tube. This was true whether the sample was frozen slowly as described earlier or rapidly by lowering into water at room temperature.