5. *Some Physical Properties of Uranium Hexafluoride.*

By D. R. LLEWELLYN.

A number of physical constants of uranium hexafluoride are determined. The density of the liquid was measured between 65° and 100° and that of the vapour from 0° to 100°. The specific heat was determined from −60° to +100° and the data were used, together with the vapour-pressure measurements from −15° to +100°, to calculate a vapour-pressure equation for solid and liquid. The critical temperature, melting point, and heat of melting are recorded. The viscosity, surface tension, and refractive index of the liquid were measured between 65° and 100°. The thermal conductivity of the vapour was measured at 5° and 105°, and the viscosity over a temperature range 0—200°. The heat of vaporization of solid and liquid, Sutherland's constant, the mean free path, the parachor, and the molecular refraction have been calculated.

URANIUM HEXAFLUORIDE was first prepared by Ruff (*Ber.*, 1909, **42**, 495) who described it as a pale yellow, hygroscopic, very reactive substance, and a strong fluorinating agent. A preliminary investigation of its chemical properties confirmed its fluorinating ability but showed that, by following the precautions and techniques now described, the pure substance could be handled satisfactorily in glass apparatus.

Uranium hexafluoride is rapidly hydrolysed by water with the formation of uranyl fluoride and hydrogen fluoride (cf. Amphlett, Mullinger, and Thomas, *Trans. Faraday Soc.*, 1948, **44**, 927). This was very troublesome because glass, in the presence of only minute traces of water or hydrogen fluoride, was severely etched by the hexafluoride, probably owing to the reactions $UF_6 + 2H_2O \longrightarrow UO_2F_2 + 4HF$ and $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$. Either of these reactions can initiate the chain.

Ruff states erroneously that the hexafluoride combines vigorously with potassium or sodium fluoride. Presumably his salts were imperfectly dried, because experiments have shown that uranium hexafluoride can remain in contact with these salts for long periods with only an initial colour change from white to very pale yellow. Addition of potassium fluoride to a UF_6–HF mixture in glass apparatus breaks the decomposition chain reaction.

Special attention was paid to reactivity of the hexafluoride towards metals and its behaviour in the presence of certain organic compounds—particularly waxes and oils used in high-vacuum technique.

Corrosion tests were carried out on a number of metals and alloys. Nickel, copper, and brass were apparently unattacked after long exposure to the vapour at room temperature. At higher temperatures, copper and brass, which would withstand attack at 100° for limited periods, were not as resistant as nickel, which was apparently unattacked after many weeks' exposure under the same conditions. Mercury at room temperature rapidly became coated with a black film.

Uranium hexafluoride was very reactive towards most organic compounds. In general, it was reduced to the tetrafluoride, hydrogen fluoride was evolved, and a carbonaceous mass deposited. The reaction with Apiezon grease " L " was slow, and this grease, when not contaminated with water, was a satisfactory lubricant for taps. Dried and degassed Apiezon oil " A " was only slowly attacked, but the reaction was too rapid to allow the use of this oil in manometers in contact with uranium hexafluoride. Apiezon waxes " W " and " W100 " were not visibly attacked at room temperature and could be used for joining metal to glass, although wherever possible this was accomplished through a copper–glass seal.

The determination of the several physical properties is described below. When this work was started no reliable data on the properties of uranium hexafluoride had been published, but various publications have since recorded certain properties. These are noted, and the results compared with those reported here, chiefly in the discussion of the data (p. 34).

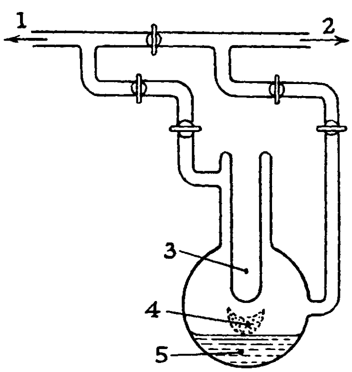
EXPERIMENTAL

The uranium hexafluoride was handled at 10^{-5} mm. The pressure in the main pumping line was indicated continuously by a Pirani gauge, calibrated at frequent intervals against a McLeod gauge (to detect any sudden change in its characteristics occasioned by corrosion of the filament by uranium hexafluoride). Once assembled, the apparatus was kept under a high vacuum whenever possible. Before the introduction of uranium hexafluoride, all accessible parts were heated with a flame and pumping was continued for at least 10 days.

The large coefficient of expansion of uranium hexafluoride between −180° and room temperature would not permit the solid to be condensed at a low temperature on to the concave surface of a normally shaped vessel, but a collecting vessel of the type shown in Fig. 1, with the condensing agent in the re-entrant tube, was satisfactory. The entrance and exit to this storage vessel were controlled by two taps in series. The inner taps were only closed in order to regrease the remainder.

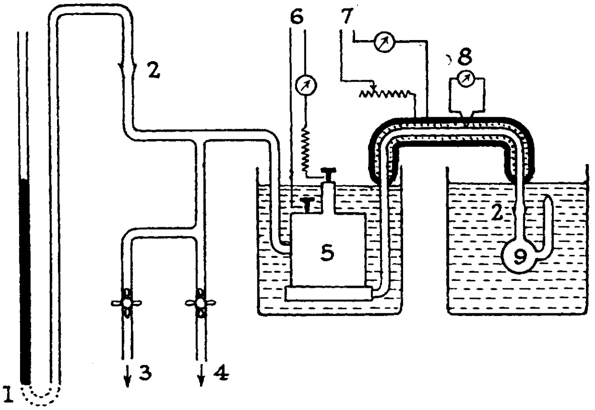
When it was necessary to have a large quantity of the hexafluoride in a vessel of normal shape it was usually convenient to transfer it in the liquid phase. The apparatus to be filled was sealed on to a vessel with a re-entrant tube, and excess of fluoride was distilled into this vessel which was then sealed off from the main reservoir. The vessel and adjoining apparatus were immersed in a thermostat at 70°, and the molten hexafluoride poured from the vessel to the apparatus, which was then cooled and sealed off.

FIG. 1.



1, *To pumps.*
2, *To apparatus.*
3, *Condensing agent.*
4, *Uranium hexafluoride.*
5, *Potassium fluoride.*

FIG. 2.



1, *Mercury manometer.*
2, *Copper–glass seals.*
3, *To pumps.*
4, *To compressed air supply.*
5, *Bellows manometer (null instrument).*
6, 2-v *Supply.*
7, 230-v *Supply.*
8, *Thermocouple.*
9, *Glass bulb for uranium hexafluoride.*

Uranium hexafluoride was received in glass vessels fitted with mechanical breakers. Hydrogen fluoride, which may have been present, or formed by reaction with water or organic material, was removed by introducing into all reservoirs a quantity of carefully dried and degassed potassium fluoride. The chief impurities were silicon tetrafluoride and freshly liberated hydrogen fluoride, both of which have appreciable vapour pressure at −20°. All samples of hexafluoride were purified by repeated distillation into reservoirs at this temperature, and the purity tested by analysis for uranium content, and by taking the vapour pressure at 0°.

Density.—(i) *Liquid* (70—100°). The density of liquid uranium hexafluoride was determined by sealing a known weight in a calibrated tube, and measuring the volume at various temperatures. A Pyrex tube, 25 cm. long and of 1 mm. internal diameter, was chosen for its uniform bore, and a bulb of 3 cm. diameter blown on one end. The capacity of the bulb and bore of the capillary were determined by distilling into them various amounts of mercury and determining the distance of the meniscus from the base of the bulb at different temperatures for each weight of mercury. The bulb was filled with liquid uranium hexafluoride at 105° as described above, and, after cooling, the top of the capillary was sealed. The position of the meniscus was determined between 70° and 100°. The weight of the hexafluoride was obtained by breaking the capillary and rapidly distilling out the contents. The determination was repeated with various samples of uranium hexafluoride. The results were as shown below, values at round temperatures being given on p. 36.

Temp.	68·0°	71·6°	74·0°	76·0°	78·2°	81·8°	84·0°	87·8°	91·6°	93·8°	98·6°	98·9°
d, g. cm.$^{-3}$	3·620	3·582	3·581	3·560	3·542	3·525	3·520	3·484	3·455	3·448	3·427	3·416

(ii) *Vapour* (0—100°/0—20 mm.). Two 4-l. flasks were joined and immersed in a thermostat. Gaseous connection was made through narrow-bore leads to a bellows manometer (cf. Kuhn and East, *J. Sci., Instr.*, 1946, **23**, 185) and a detachable weighing tube. Uranium hexafluoride was introduced into the bulb and, after 30 min. had been allowed for temperature equilibrium to be attained, the pressure was recorded and then decreased by surrounding the weighing tube with solid carbon dioxide–alcohol. Results were as follows :

Temp.	18·0°	56·0°	83·0°	96·0°
Pressure range, mm.	1·76—17·90	0·89—18·22	0·31—1765	0·03—1090
Mean value of *M*	352 ± 1	352 ± 1	352 ± 1	352 ± 1

Vapour Pressure ($-15°$ to 100°).—(*a*) The vapour pressure between 0° and 100° was measured by means of the apparatus shown in Fig. 2. The glass bulb 9 was connected to the inside of the bellows through a copper–glass seal, and the connecting tube wound with nichrome wire and well lagged. After being thoroughly degassed, uranium hexafluoride was distilled into the bulb, which was then sealed off. The temperature of the manometer and connecting tube was raised to 100° and kept thereat for about 1 hour before measurement of the external pressure corresponding to the make and break of the electrical circuit. The determinations were carried out with frequent changes of hexafluoride. Results are appended :

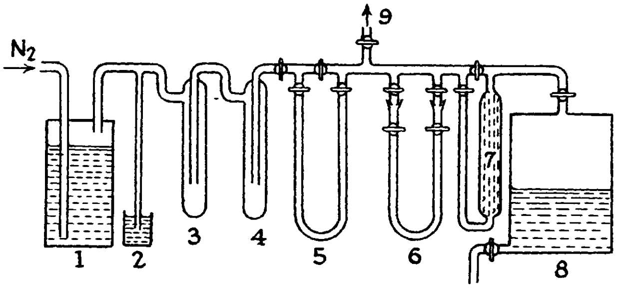


FIG. 3.

1, *Sulphuric acid bubbler.*
2, *Safety bubbler.*
3 *and* 4, *Liquid-air traps.*
5, U-*Tube containing* UF_6.
6, *Detachable* U-*tube.*
7, P_2O_5 *guard tube.*
8, *Aspirator.*
9, *To pumps and main* UF_6 *reservoir.*

Temp.	Press., mm.	Temp.	Press., mm.	Temp.	Press., mm.	Temp.	Press., mm.	Temp.	Press., mm.
0·0°	17·9	20·5°	83·1	46·2°	423·4	69·7°	1338	83·5°	1970
5·3	27·4	24·6	109·6	50·0	520·2	70·0	1350	85·0	2058
7·9	32·9	30·8	164·4	54·1	656·2	72·8	1470	89·3	2300
10·0	39·2	32·5	196·2	58·0	806·2	75·0	1566	95·0	2648
13·3	49·6	37·6	251·2	62·9	1042	79·1	1752	100·0	2985
18·7	73·1	43·0	356·0	64·8	1161	82·0	1905		

Values at each degree from 0° to 65° and from 65° to 100° are given on p. 35.

(*b*) Between 0° and $-15°$ the vapour pressure was measured by a dynamic method. The apparatus (Fig. 3) was thoroughly degassed, and uranium hexafluoride condensed in the U-tube (5) by slowly immersing it in an ice–water mixture. Dry nitrogen was drawn over the fluoride by running water from the aspirator, and the hexafluoride condensed out and weighed in the U-tube (6). The determination was repeated, for different samples, and different rates of nitrogen flow, with the U-tube (5) at 0° or $-15°$. The results were :

Temp.	$-14·8°$	0·0°
V. p., mm.	5·13 ± 0·03 (mean of 5 values)	17·81 ± 0·03 (mean of 5 values)

Critical Temperature.—The hexafluoride was distilled into a Pyrex tube about 10 cm. long and 3 cm. in internal diameter. The sealed-off tube was attached by wire to a thermometer and supported in a heated glass tube. The temperature was slowly increased until all the liquid had disappeared. Successive lengths of 2 cm. were sealed off until it was observed, on raising the temperature, that the meniscus disappeared suddenly from midway up the tube. The temperature of disappearance and reappearance of the meniscus was observed for a number of tubes. The critical temperature was thus found to be 245° ± 5°

Specific Heat (−60° to +100°).—A copper calorimeter was made from a cylinder, of 8 mm. internal diameter and 5 cm. long, and connection made to it through a copper capillary tube of 1 mm. internal diameter. The calorimeter was covered with a thin layer of insulating material and wound with 2 m. of 36-gauge enamelled Eureka wire; between these turns a platinum wire was wound for measuring temperature. The resistance thermometer was calibrated by surrounding it in turn with solid carbon dioxide, ice, and steam.

The calorimeter was filled with liquid uranium hexafluoride by attaching it through a copper–glass seal to a small re-entrant trap as previously described. Care was taken to see that the temperature of the system was a little above 100°. When full, the copper capillary was squeezed tightly in a vice and the calorimeter allowed to cool. The capillary was cut in the middle of the squeezed portion and both parts were rendered vacuum-tight by a little soft solder. The calorimeter was suspended by its leads in a wide (5 cm.) silvered tube which could be evacuated and surrounded by a thermostat.

The heater circuit was completed through a 4-v. accumulator, a variable resistance, an ammeter, and an automatic time switch. A high-resistance voltmeter was connected across the heater. The procedure was as follows. The calorimeter was brought to the required temperature, and after evacuation of the tube surrounding the calorimeter, the resistance of the platinum thermometer was taken at 1-min. intervals during 10 min.; the heating current was then switched on for 4 min., the watts absorbed being obtained from the readings of the voltmeter and ammeter in the heating circuit. At the end of the heating period the resistance of the platinum thermometer was again recorded at 1-min. intervals for 10 min. The effective change in resistance (d*R*) during the heating period was obtained from a resistance–time graph. Heat exchanges between the calorimeter and its surroundings were estimated from the slope of the curves before and after heating.

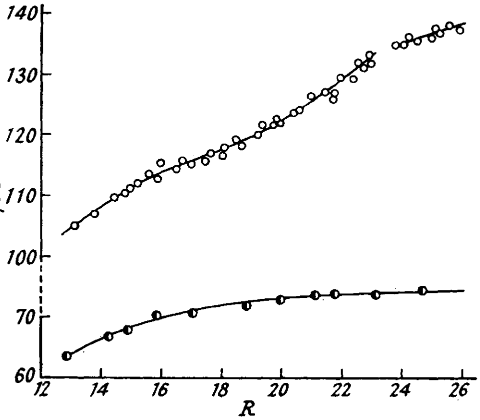


FIG. 4.
○ *Calorimeter and* UF$_6$.
◐ *Empty calorimeter.*

When sufficient values of the heat capacity of the full calorimeter had been obtained for temperatures between −60° and 100° it was weighed and then emptied. The heat capacity of the empty calorimeter was determined as before. Graphs were drawn connecting $J/\mathrm{d}R$ and R, where J is the input energy in joules corresponding to a change of resistance dR at the mean resistance R.

A subtraction of these curves (Fig. 4) gives a relation between $J/\mathrm{d}R$ and R for the sample of hexafluoride alone. From this curve, the weight of hexafluoride used, and the calibration curve for the resistance thermometer, the heat capacity was calculated. A correction was applied for the heat used in evaporating solid or liquid when the calorimeter was not full.

Two further samples of uranium hexafluoride were used. The weight of material used was constant and the results have been plotted together. They are tabulated at round values of temperature on p. 34, the estimated error being ±1%.

Melting Point and Heat of Melting.—The apparatus used was that described in the preceding section. The calorimeter was heated continuously from 20° to 100°. The graph connecting temperature with time showed a horizontal portion corresponding to a m. p. at 64·9°. This temperature was confirmed by heating a sample in a sealed glass tube.

The heat of fusion (4550 cal. mol.$^{-1}$) was calculated from the length of the horizontal portion and a knowledge of the heat input. Corrections were applied for heat losses due to radiation and conduction along the leads.

Viscosity.—(1) *Liquid* (70—100°). An Ostwald viscometer was sealed on to a small re-entrant trap and filled to two-thirds of its capacity with liquid by the method previously described, then cooled and sealed off. The viscometer was immersed in a glass thermostat and supported by a device which permitted rotation through 180° about a horizontal axis. The bath was kept at 70° for 30 minutes, after which the viscometer was tilted so that liquid flowed into and filled the smaller bulb. It was then returned to the vertical, and the time taken for the liquid to fall between the two predetermined marks was measured. This procedure was repeated at a number of temperatures between 70° and 100°, and after the exact depth of liquid had been marked, the tip was broken off and the viscometer emptied. The constant for the viscometer for the particular quantity of liquid used was determined by repeating the experiment with the same volume of purified alcohol and water. Finally, the determination was repeated with different samples and volumes of uranium hexafluoride. The results were :

Temp.	67·9°	70·0°	71·5°	73·9°	74·5°	76·5°	78·8°
$10^2\eta$ (poises)	0·924	0·910	0·902	0·892	0·880	0·876	0·870
Temp.	83·3°	84·9°	88·3°	92·2°	95·7°	97·8°	99·0°
$10^2\eta$ (poises)	0·834	0·832	0·815	0·794	0·770	0·766	0·752

Values at round temperatures are given on p. 36.

(ii) *Vapour* (0—200°). A Pyrex capillary tube, 17·5 cm. long, was selected for uniform bore. One end was connected through a fine-control bellows-valve to a uranium hexafluoride reservoir and a bellows manometer; the other was also connected to a bellows manometer and through a change-over tap to two small condensing vessels, one of which could be removed from the apparatus and weighed. The capillary was surrounded by a hot-air bath with thermocouples distributed to ensure a uniform temperature.

The viscosity was calculated from the formula

$$\eta = \frac{\pi r^4(p_1^2 - p_2^2)t\rho(1 + 4\xi/r)}{16lm(p_1 + p_2)/2} - \frac{m(1\cdot12 + \ln p_1/p_2)}{8\pi tl}$$

where r = radius of capillary; $p_1 - p_2$ = the pressure difference between the ends of the capillary; ρ = mean density of vapour; m = mass of vapour flowing in t seconds; l = length of capillary. The " slip " correction ($4\xi/r$), where ξ is approximately equal to the mean free path, at the mean pressure, was less than 1%. The second term was less than 0·5%.

Temp.	20·0°	65·0°	94·0°	128·0°	166·0°
$\eta \times 10^4$ (poises)	1·76 ± 0·03	1·94 ± 0·03	2·08 ± 0·03	2·24 ± 0·03	2·57 ± 0·03

The results, each the mean of 5 measurements, were as follows (values at round temperatures on p. 36) :

Thermal Conductivity. Vapour (5° *and* 105°).—The thermal conductivity was determined by comparing the heat loss from an electrically heated wire confined in a co-axial cylinder, when surrounded by air and by uranium hexafluoride severally. Gregory and Archer (*Proc. Roy. Soc.*, 1926, *A*, **110**, 91) have given equations for the heat loss from two wires, identical in all respects except length. It is shown that two wires of length l_1 and l_2 incorporated in a Callendar–Griffiths bridge as in Fig. 5 may be treated as an ideal length of wire ($l_1 - l_2$) having uniform temperature and no end corrections. The heat loss from this wire may be written as

$$C^2R = 2\pi Kl\theta/\log(r_2/r_1) + \phi + \psi$$

where C = heating current; R, l, and θ = resistance, length, and temperature of wire, respectively; r_1 and r_2 = radius of wire and tube respectively; ϕ = heat loss by convection; ψ = heat loss by radiation; K = thermal conductivity of the surrounding vapour.

Following previous workers, using the hot wire method, ϕ was eliminated by working at pressures sufficiently low for it to be neglected; ψ was determined by measuring the heat loss when the tubes were evacuated. The variable resistance r (Fig. 5) used to balance the bridge corresponds to the length of wire $l_1 - l_2$, so that as long as r remained constant and the bridge balanced, the resistance, and consequently the temperature of the ideal length of wire of length l, remained constant.

If $C_{vac.}$, C_{air}, and C_{UF_6} are the currents necessary to balance the bridge when the tubes are evacuated, or filled with air or with hexafluoride, then the ratio of the conductivities is given by

$$\frac{K_{air}}{K_{UF_6}} = \frac{C_{air}^2 R - C_{vac.}^2 R}{C_{UF_6}^2 R - C_{vac.}^2 R}$$

The tubes were made of nickel of ½″ internal diam., one 8″ long and the other 4″ long. The nickel wires were 0·05″ in diameter, and insulated from one end of the tube. For temperatures around 0° this could be done by an insulating washer rendered vacuum-tight by Apiezon wax W. For temperatures around 100°, the nickel wire was attached to a tungsten wire sealed through the glass of a copper–glass seal. Great care was taken to ensure that the size and resistance of the ends were identical, and many pairs were made before the desired similarity was produced.

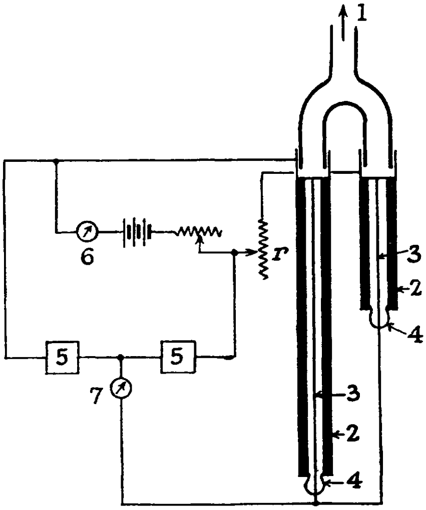


FIG. 5.

1, *To pumps and* UF_6 *reservoir.*
2, *Nickel tubes.*
3, *Nickel wires.*
4, *Tungsten–glass seals.*
5, 5,000 w *resistance.*
6, *Ammeter.*
7, *Galvanometer.*

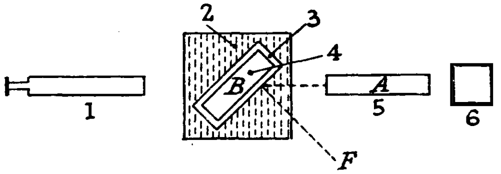


FIG. 6.

1, *Telescope.*
2, *Uranium hexafluoride.*
3, *Glass.*
4, *Air.*
5, *Collimator.*
6, *Slit and source of light.*

When full of air at atmospheric pressure, the tubes were surrounded by a thermostat, and, a very small bridge current being used, the value of *r* to balance the bridge was found for various temperatures of the thermostat between 0° and 120°.

To compare the conductivities of air and uranium hexafluoride the thermostat was set at 0° and *r* chosen to correspond to a wire temperature of about 10°. The bridge was then balanced by varying the current with the tubes (*a*) evacuated, (*b*) surrounded by air, (*c*) surrounded by hexafluoride. For each condition a series of readings was taken at different pressures. The balancing current increases from $C_{vac.}$ when the tubes are evacuated to a constant value C_{air} or C_{UF_6} which increases only when convectional losses become appreciable.

Measurements were made for different values of *r* and the thermostat was then raised to 100°. The value of the conductivity of carbon dioxide measured at the lower temperature was within 0·5% of the value reported in the International Critical Tables. Results are given on p. 36.

Refractive Index (*Liquid*, 70—100°).—The methods available for determining the refractive index of liquid uranium hexafluoride were very limited because the properties of the liquid necessitate an apparatus which can be heated above 65° and withstand a pressure of 3 atm. The method which finally proved satisfactory was that involving the optical system shown in Fig. 6. An air cell immersed in the liquid could be rotated about a vertical axis between the telescope and collimator. By rotating the cell at right angles to the beam of light a position can be reached when the field of vision is divided into light and dark sections. At this point, which is well defined, total internal reflection takes place and it can be shown that $\mu(\text{air/liq.}) = 1/\sin ABF$.

The cell was constructed by fusing together the perimeters of two circular Pyrex glass plates, $1\frac{1}{2}$ mm. thick, and of 2 cm. diameter. A glass tube was sealed to one part of the perimeter, through which the cell could be evacuated and tested for leaks. When free from leaks, the cell was sealed off and supported in the centre of a glass tube, $2\frac{1}{2}$ cm. in diameter, attached to a re-entrant trap. The glass cell was then covered with liquid hexafluoride and, after being cooled and sealed off from the trap, the outer glass tube was mounted in a brass cylinder connected through a universal joint to a vernier pointer moving over a horizontal scale. The universal joint was clamped when the cell rotated about its vertical axis. A thermostat with parallel glass sides was brought into position around the tube, and the telescope and collimator adjusted.

Two series of readings were taken, one with a sodium lamp and one with a mercury-vapour lamp and filter. At various temperatures between 70° and 100° the four positions of the cell for which the field of vision was divided were recorded and the refractive index calculated.

Wave-length of light 5890 Å.

Temp.	69·4°	72·2°	73·5°	77·5°	85·2°	87·2°	90·5°	95·1°
μ	1·367	1·366	1·367	1·360	1·353	1·354	1·350	1·347

Wave-length of light 4360 Å.

Temp.	66·0°	68·0°	72·3°	75·2°	79·2°	84·0°	84·7°	90·5°	91·0°
μ	1·385	1·386	1·382	1·377	1·376	1·371	1·369	1·364	1·364

Values at round temperatures are given on p. 36.

Surface Tension (70—100°).—The ends of two similar Pyrex capillary tubes and a third tube of narrow diameter (0·5 mm.) were connected together with two pieces of wide-bore tubing, sealed to a small re-entrant vessel. The diameters of the tubes were found by measuring the capillary rise in each of (*a*) pure redistilled alcohol and (*b*) ether. The apparatus was then filled with liquid hexafluoride in the usual way. The differences in heights between the hexafluoride meniscus in (i) each of the two capillary tubes and (ii) the third tube were determined at different temperatures, from which values of the surface tension were calculated.

The contact angle was determined by pouring liquid hexafluoride on a flat glass plate in an evacuated vessel. The angle was too small to be measured, and the correction for the shape of the meniscus was taken to be zero.

The values obtained are given on p. 36.

DISCUSSION

Molecular Weight.—Found: 352 ± 1. Calc.: 352·1. Amphlett, Mullinger, and Thomas (*loc. cit.*) obtained a similar value for measurements up to 50° over a pressure range of 5—500 mm.

Critical Data.—Critical temperature = 245° ± 5°. The value calculated from the Ramsay–Shields equation and the measured values of the surface tension is 235° ± 20°. On the assumption that at the critical temperature the viscosities of liquid and vapour are equal, this temperature is again found to be 235°. In view of the large extrapolations involved these values are not very significant.

Triple-point Data.—These are found to be: temperature (p. 31), 64·9°; vapour pressure (p. 30) 1161 mm.; density of liquid (p. 30), 3·63 g. cm.$^{-3}$; heat of fusion (p. 31), 4550 cal. mol.$^{-1}$.

Specific Heat.—The values for the solid agree with those reported by Brickwedde, Hoge, and Scott (*J. Chem. Phys.*, 1948, **16**, 429) at −50° and +30° but there is a maximum difference of ~5% at 60°. The values for the liquid are in poor agreement and differ by about 5% at 100°, which is large even when the difficulties of handling the material are taken into consideration.

Temp.	−50°	−40°	−20°	0°	20°	40°	60°	70°	80°	90°	100°
C, cal. mol.$^{-1}$ deg.$^{-1}$	34·2	34·6	35·7	37·0	39·0	41·8	44·5	47·4	48·1	48·8	49·5

The specific heat of the gas was measured by H. S. Arms (personal communication) and the following values were obtained :

Temp.	25°	75°	125°
C_p, cal. mol.$^{-1}$ deg.$^{-1}$	33·5 ± 1	34·5 ± 1	35·3 ± 1

Values calculated from an analysis of the infra-red spectroscopic data (Bigeleisen and Mayer, *J. Chem. Phys.*, 1948, **16**, 443) are lower by 5% and extend over a larger temperature range. From Arms's values, extrapolated with the help of the spectroscopic data, the following values have been obtained :

$$C_p\text{ (solid)} - C_p\text{ (vapour)} = (e^{-2560/T} + 21{\cdot}53)/T^2 + 2\text{ cal. mol.}^{-1}\text{ deg.}^{-1}$$
$$C_p\text{ (liquid)} - C_p\text{ (vapour)} = 0{\cdot}045T - 1{\cdot}85\text{ cal. mol.}^{-1}\text{ deg.}^{-1}$$

Vapour Pressure.—(i) The vapour pressure of the solid at $T°$ K is given by

$$\log P = \int_0^T \frac{\lambda_0}{\boldsymbol{R}T^2}\,\mathrm{d}T - \int_0^T \frac{\mathrm{d}T}{\boldsymbol{R}T^2}\int_0^T\left(\frac{e^{-2560/T} + 21{\cdot}53}{T^2} + 2\right)\mathrm{d}T$$

where λ_T = heat of vaporization of the solid at $T°$/K. Integrating, and calculating the values of the integration constants from the measured values of temperature and pressure, we get

$$\log_{10} P_{\text{mm.}} = -2751/T - 75{\cdot}0\,e^{-2560/T} - 1{\cdot}01\log_{10} T + 13{\cdot}797$$

Vapour pressure, mm.

Temp.	0°	−1°	−2°	−3°	−4°	Temp.	0°	−1°	−2°	−3°	−4°
−15°	5·00	4·52	4·12	3·76	3·42	−5°	11·9	10·9	10·0	9·18	8·43
−10	7·73	7·08	6·49	5·93	5·42	0	17·9	16·5	15·2	14·0	12·9

Temp.	0°	1°	2°	3°	4°	Temp.	0°	1°	2°	3°	4°
0°	17·9	19·4	21·0	22·8	24·6	35°	215	229	244	259	275
5	26·6	28·8	31·1	33·5	36·1	40	292	310	330	350	371
10	39·0	42·0	45·2	48·6	52·4	45	394	417	442	468	494
15	56·2	60·4	64·9	69·7	74·8	50	522	552	583	617	652
20	80·2	85·9	92·0	98·6	105·4	55	689	726	766	807	851
25	112·7	120·5	128·8	137·7	146·9	60	897	946	998	1047	1104
30	157	167	178	190	202	65	1161				

(ii) By a similar procedure the following equation has been derived for the vapour pressure of the liquid :

$$\log_{10} P_{\text{mm.}} = -1946/T - 0{\cdot}00492T + 0{\cdot}934\log_{10} T + 8{\cdot}123$$

Vapour pressure, mm.

Temp.	0°	1°	2°	3°	4°	Temp.	0°	1°	2°	3°	4°
65°	1161	1190	1235	1270	1310	85°	2050	2105	2160	2220	2280
70	1350	1390	1430	1480	1520	90	2330	2390	2460	2520	2580
75	1560	1610	1650	1700	1750	95	2650	2710	2780	2840	2910
80	1790	1840	1890	1950	2000	100	2980				

Values for the vapour pressure of the solid from 12° to 50° reported by Amphlett, Mullinger, and Thomas (*loc. cit.*) lie on either side of the formula values but do not show the deviation from the linear relation between log p and $1/T$. Those reported by Crist and Weinstock (*J. Chem. Phys.*, 1948, **16**, 436) agree within 1·5%, their data lying above the formula values.

Latent Heats.—Heat of sublimation (*solid*). Calculated from specific-heat and vapour-pressure measurements by the following formula, these are found to be :

$$\lambda_T = 12{,}600 - 875{,}600\,e^{-2560/T} - 2T\text{ cal. mol.}^{-1}$$

Temp.	−50°	−25°	0°	20°	40°	60°	65°
λ_T, cal. mol.$^{-1}$	12,145	12,075	11,980	11,870	11,730	11,530	11,470

Estimated error = ± 1%.

Heat of evaporation (*liquid*). The formula deduced from specific-heat and vapour-pressure measurement is

$$\lambda_T = 8890 - 0{\cdot}0225T^2 + 1{\cdot}85T\text{ cal. mol.}^{-1}.$$

This formula does not satisfy the condition that $\lambda_T = 0$ at the critical temperature and the empirical formula

$$\lambda_T = 6920 - 5{\cdot}3(t - 65) - 0{\cdot}184(t - 65)^2 \text{ cal. mol.}^{-1}$$

where t is the centigrade temperature, has been obtained which agrees with the first formula over the measured range and does satisfy the condition that $\lambda_T = 0$ at 245°. The results (estimated error ±1%) are :

Temp.	65°	70°	90°	110°
λ_T, cal. mol.$^{-1}$	6920	6890	6670	6310

The heats of sublimation and evaporation have been measured by Masi (*J. Chem. Phys.*, 1949, **17**, 755) and values for the solid are within 1% of those calculated above; those for the liquid differ by 2% at 100°. The values at the triple point are 11,429 and 6859 cal. mol.$^{-1}$, giving 4570 cal. mol.$^{-1}$ for the heat of fusion, in excellent agreement with the value 4550 ± 50 cal. mol.$^{-1}$ reported on p. 31.

Density.—Liquid. Values at round temperatures are :

Temp.	65°	70°	80°	90°	100°
d, g. cm.$^{-3}$	3·63	3·60	3·54	3·48	3·41

The density at the triple point was found by H. F. Priest (OSRD Report, A 139) to be 3·607 g. cm.$^{-3}$. The density has also been measured by the falling-drop method (Hoge and Wechsler, *J. Chem. Phys.*, 1949, **17**, 617) and the values reported are within 0·5% of those given above. At the triple point the value by this method is 3·624 g. cm.$^{-3}$.

Viscosity.—Liquid. Values at round temperatures (estimated error ± 1%) are :

Temp.	70°	80°	90°	100°
$10^3\,\eta$ (poises)	9·1	8·5	8·0	7·5

Vapour. $\eta = 1{\cdot}67(1 + 0{\cdot}0026t) \times 10^{-4}$ poise (±2%)

Temp.	0°	20°	50°	100°	150°	200°
$10^4\,\eta$ (poises)	1·67	1·76	1·89	2·11	2·33	2·55

Sutherland's constant calculated from these data is 101. The mean free path at 0° is $1{\cdot}27 \times 10^{-3}$ cm. at 1 mm.

Thermal Conductivity of Vapour.

Temp.	5°	105°
$K \times 10^5$, cal. deg.$^{-1}$ cm.$^{-1}$ sec.$^{-1}$	1·42	1·94

Estimated error = ± 1%.

Surface Tension.—The parachor, based on the following values, is 200 ± 1.

Temp.	70°	80°	90°	100°
γ, dyne cm.$^{-1}$	16·8	15·6	14·3	13·1

Estimated error = ± 1%.

Refractive Index.—Liquid. Values at round temperatures are :

Temp.	70°	80°	90°	100°
μ at 4360 Å	1·383	1·374	1·365	1·355
μ at 5890 Å	1·367	1·358	1·350	1·342

From these values the molecular refraction is : $[R]^{85}_{4360} = 22{\cdot}59 \pm 0{\cdot}1$, $[R]^{85}_{5890} = 21{\cdot}83 \pm 0{\cdot}1$.

Vapour. Calculated on the assumption that the molecular refraction of the vapour is the same as that of the liquid, the index of refraction of the vapour is given by $n - 1 = 5{\cdot}2 \times 10^{-4}p/T$, where p is pressure in mm. and T the absolute temperature.

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The Clarendon Laboratory,
Parks Road, Oxford.

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