302. *Some Physical Constants of Methyl Fluoride, and the Atomic Weight of Fluorine.*

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VERY few investigations on the atomic weight of fluorine by determination of the limiting density of its gaseous compounds have been made. This appears to be due chiefly to the fact that many of these compounds are not easy to prepare pure, and have been very little studied, whilst those containing a large percentage of fluorine can in many cases only be produced by interaction with gaseous fluorine.

One such compound, *viz.*, methyl fluoride, can, however, be readily prepared by various methods, of which the three most important are the interaction of potassium methyl sulphate and potassium fluoride or of methyl sulphate and silver fluoride; and the action of heat on tetramethylammonium fluoride (Collie, J., 1889, **55**, 110). The limiting density of methyl fluoride, prepared by the first two methods, has been investigated by Moles and Batuecas (*J. Chim. physique*, 1920, **18**, 353). The gas was weighed at various pressures in bulbs, and the limiting density obtained by extrapolation. This work led to an atomic weight of fluorine of 18·998, whilst the compressibility of the gas $(1 + \lambda)$ was found to be 1·018.

We have repeated this work, using a buoyancy microbalance. The method consists essentially in finding the ratio of the pressures at which two gases, *e.g.*, oxygen and methyl fluoride, have the same density. These ratios are determined for two or more different densities, and the limiting value of the ratio at zero pressure is found by extrapolation. This value is inversely proportional to the molecular weights of the gases. The details of the method have been previously described (Whytlaw-Gray, Patterson, and Cawood, *Proc. Roy. Soc.*, *A*, 1931, **134**, 7).

The gas used in our preliminary investigations on the limiting density of methyl fluoride (*Nature,* 1931, **128**, 375) was made by the third of the above methods, since the other two might give rise to a gas contaminated with dimethyl ether. Working in this way at 21°, we obtained the following data for the pressures at which methyl fluoride and oxygen have the same density.

	p_{O_2}.	p_{CH_3F}.	p_{O_2}/p_{CH_3F}.	Mean.
(A)	$156{\cdot}87_5$	$147{\cdot}22_7$	1·06553	1·06550
	$156{\cdot}83_4$	$147{\cdot}19_8$	1·06546	
(B)	$333{\cdot}02_5$	$312{\cdot}05_4$	1·06721	1·06726
	$338{\cdot}18_8$	$316{\cdot}85_8$	1·06731	

Each of these pressures is, of course, the mean of a number of readings, whilst the four ratios refer to four different fillings with each gas. If the mean values of the ratios are plotted against the corresponding pressures of oxygen or methyl fluoride and extrapolated to zero pressure, the limiting value of the ratio is found to be 1·06395, corresponding to a molecular weight of methyl fluoride of 34·046. If it be assumed that the atomic weight of carbon lies near to 12·010, a value for which we have recently obtained considerable evidence, the atomic weight of fluorine becomes 19·013. From these results it is also possible to calculate the compressibility $(1 + \lambda)$ at 21° of methyl fluoride by assuming the compressibility of oxygen. If $(1 + \lambda)$ for oxygen at 21° is taken to be 1·00074, we obtain for $(1 + \lambda)$ at 21° for methyl fluoride the figure 1·0082—this value may not be very accurate, as it is only obtained over a pressure range of 170 mm. In order to find the compressibility at 0°, it is necessary to know the coefficient of thermal expansion of methyl fluoride. This has not been determined, and accordingly we have made use of a thermal coefficient slightly higher than that of carbon dioxide, for which the value is well known. We thus obtained for the compressibility $(1 + \lambda)$ of methyl fluoride at 0° the value 1·0109, in general agreement with the compressibility of gases of similar critical constants, but entirely at variance with the figure 1·018 found by Moles and Batuecas.

Our work on methyl fluoride has been criticised by Moles (*Nature*, 1931, **128**, 966) on the ground that Collie's method does not give pure methyl fluoride, but a constant-boiling mixture containing 2% of methane. From this he concludes, not only that our molecular weight and compressibility are incorrect, but also that Collie's critical data are in error. We have already pointed out (*Nature*, 1932, **129**, 245) that there appears to be no evidence for the existence of the constant-boiling mixture. We have now redetermined (1) the critical constants, using methyl fluoride prepared both by Collie's method and also by the first method, as used by Moles, and (2) the compressibility, using methyl fluoride made by the latter method.

EXPERIMENTAL.

Preparation of Methyl Fluoride.—Pure MeF is easily obtained by Collie's method, *i.e.*, by heating NMe_4F; this was synthesised from NMe_3, which was made from paraformaldehyde and MeI free from Et compounds. The NMe_4I was transformed into $NMe_4{\cdot}OH$ by means of freshly pptd. Ag_2O. The hydroxide solution was then filtered from AgI and neutralised with pure HF, thus giving NMe_4F.

On heating the dry solid NMe_4F, equal vols. of NMe_3 and MeF are produced. The former was removed by passage first through a solid CO_2–CMe_2O freezing mixture, and then through two washing towers containing conc. H_2SO_4. The gas was further purified by bringing it into contact with liquid and solid KOH, and was then passed through a U-tube, again cooled by solid CO_2–CMe_2O. After drying over P_2O_5, the gas was solidified in liquid air and the vessel evacuated to remove any non-liquefiable gas. This MeF was fractionated 3 times and then bubbled through its own liquid. About 2 l. of highly purified gas were thus obtained. The gas was then refractionated and samples were taken of the first, middle, and last fractions. The relative densities of these 3 fractions were measured by the microbalance. The balancing pressures were respectively $312{\cdot}12_7$, $312{\cdot}05_3$, and $312{\cdot}05_5$ mm. It will be seen that the first runnings had a slightly higher balancing pressure, due probably to a trace of air. The middle and last fractions, however, agreed within the limit of error of our measurements, and were unaltered by further fractionation. These last fractions were used in determining the press. ratios given above, and have also been used for finding the crit. data of MeF. Considering the rigorous care taken to exclude Et compounds in the prep. of the gas, and the difference in b. p. (46°) between MeF and EtF, it is difficult to believe that any contamination from this source was present.

When MeF is made by the action of $KMeSO_4$ on KF, a large amount of Me_2O is produced : we obtained more Me_2O than MeF, but it is possible that by a careful study of the reaction the quantity might have been reduced. The gas was purified in a similar way to that already described, but numerous fractionations were carried out. After much difficulty about 0·5 l. of purified MeF was obtained.

Determination of the Critical Constants.—The crit. consts. were determined in a modified Andrews compressibility apparatus, kindly lent by Professor Whytlaw-Gray. The graduated capillary containing the MeF was enclosed in a glass water-jacket, wound round with Ni–Cr ribbon connected to the mains through a lamp and variable resistance. Stirring was effected by blowing a stream of bubbles through the H_2O from a cylinder of compressed air. Working in this way, it is possible by suitable adjustment of the resistance to maintain the temp. of the bath constant to $\pm$ 0·01° at any of the temps. at which we worked, or to cause it to rise or fall at a constant rate. Accurate determinations of the crit. data can therefore be made. Our manometer gauge containing air was surrounded by a similar jacket filled with ice and H_2O. The data of Otto and Holborn (*Z. Physik*, 1925, **33**, 1) were taken as our standard for the compressibility of air.

The tubes were filled by attaching them to an apparatus as shown in the fig. In order to introduce a measured quantity of air, both the gauge *A*, with its reservoir *L*, and the point burette *B* were evacuated. The three-way tap *C* was then turned so that dry air free from CO_2 could be admitted into the burette.

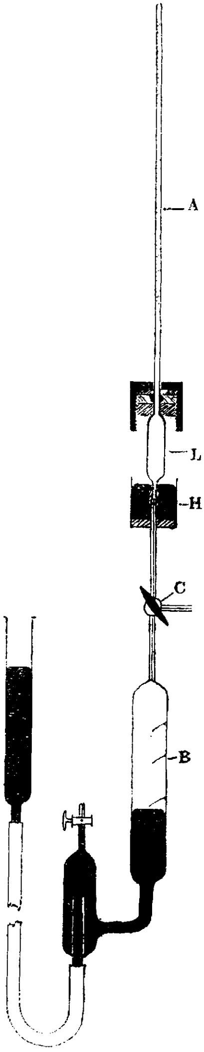
After determination of the vol., the measured air was taken up into the reservoir *L*. The mercury-sealed rubber connexion at *H* was then broken, and the drawn-down end of the reservoir placed in a special iron spoon containing Hg. The gauge was then transferred to the compression apparatus.

A similar procedure was followed when filling a tube with MeF, except that the gas was frozen once or twice in a fractionating vessel or in the tube *A* itself, and then pumped off to ensure absence of air. In the latter case the vol. was measured after determination had been made in the Andrews apparatus.

Critical temperature. This was measured by raising the temp. of the bath slightly above the crit. point, until the line of demarcation between liquid and vapour had disappeared. The bath was then allowed to cool very slowly. The temp. at which fog, as opposed to opalescence, appeared as a narrow zone in the tube was taken to be the crit. temp. Those of the gas made by both methods were identical at 44·55° within the limits of error of our measurements, *i.e.*, a few hundredths of a degree.

Critical pressure. The crit. isothermal was determined, and the crit. press. was read off when the vol. had its crit. value. This procedure is more accurate than finding the point of inflexion of the crit. isothermal, although actually the point of inflexion appeared to occur at about the crit. vol. When the crit. press. of the gas made in the two ways was measured against the same pressure gauge, exactly the same press. was obtained within the limits of accuracy of the apparatus. In order, however, to obtain a good average for the crit. press. three separate fillings of the manometer gauge with air were made, and the crit. press. was determined with each. The values obtained were 58·3, 58·1, 57·6 atm.: mean, 58·0 ± 0·2 atm.

Critical volume. The crit. vol. was determined by the method of rectilinear diameters of Cailletet and Mathias. Readings were taken at a series of temps. of the amount of liquid and vapour at two different vols.; from these data the total vol. of liquid and vapour at various temps. could be calculated, and thus, the weight of MeF being known, the rectilinear diameter could be found. By extrapolation of the diameter to the crit. temp., the crit. density and hence the crit. vol. were obtained. The wt. of MeF was found by making use of our previously determined wt. of 1 l. at 21° and 76 cm. Since our measurements of the vol. were made at 20°, the temp. correction required was very small. The following are the results obtained for the gas made by the two different methods.



	Density of		Mean density,		
Temp.	liquid.	vapour.	obs., $\rho_{obs.}$.	calc., $\rho_{calc.}$.	$\rho_{obs.} - \rho_{calc.}$.
(1) *Methyl fluoride made by heating tetramethylammonium fluoride.*					
44·55°	—	—	—	0·3027	—
43·00	0·4204	0·1860	0·3032	0·3045	− 0·0013
42·00	0·4388	0·1727	0·3058	0·3055	+ 0·0003
40·02	0·4575	0·1588	0·3082	0·3076	+ 0·0006
35·02	0·4945	0·1339	0·3142	0·3131	+ 0·0011
30·02	0·5290	0·1089	0·3190	0·3186	+ 0·0004
20·67	0·5763	0·0794	0·3297	0·3288	− 0·0009
(2) *Methyl fluoride made from potassium methyl sulphate and potassium fluoride.*					
44·55	—	—	—	0·2981	—
43·98	0·3828	0·2160	0·2994	0·2989	+ 0·0005
43·00	0·4063	0·1926	0·2995	0·3001	− 0·0006
42·00	0·4219	0·1793	0·3006	0·3014	− 0·0008
40·02	0·4525	0·1537	0·3031	0·3041	− 0·0010
35·02	0·4951	0·1287	0·3119	0·3107	+ 0·0012
30·02	0·5332	0·1056	0·3194	0·3172	+ 0·0022
20·04	0·5781	0·0794	0·3287	0·3303	− 0·0016

The straight lines connecting temp. (t) and mean density (ρ) obtained by the method of least mean squares from the observations are respectively :

$$(1)\ \rho = 0{\cdot}3513 - 0{\cdot}0011t \text{ and } (2)\ \rho = 0{\cdot}3565 - 0{\cdot}0013t.$$

The calc. mean densities were obtained by substitution for the various temps. in these formulæ. The values of the crit. density are accordingly 0·3027 and 0·2981 g./c.c., respectively : the difference lies within the limit of experimental error. The crit. density of MeF is therefore 0·300 g./c.c., and the crit. vol. 3·33 c.c./g. The crit. vol. may also be expressed as the vol. which 1 c.c. of the gas at N.T.P. would occupy at the crit. temp. and press., *viz.*, 0·00506 c.c.

An examination of the above tables shows that Cailletet and Mathias's law is obeyed within the limit of error of our experiments, no curvature being shown by the mean diameter. The mean slope of the line is −0·0012, which lies within the limits −0·0005 to −0·0023 shown by most substances.

Critical coefficient. The value of the ratio RT_c/P_cV_c is 3·96, in general agreement with that for other substances of similar constitution.

Compressibility of Methyl Fluoride.—In order to determine the compressibility coeff. A of MeF, measurements of the compressibility were made in the compression apparatus between pressures of about 1 and 3 m. The *pv–p* curve thus obtained was extrapolated to zero press. in order to find the compressibility between 0 and 1 atm.

A few preliminary measurements were made in capillaries of 1·5 mm. bore, but most were carried out in tubes of 4·5 mm. bore. The latter were used, as it was feared that the measurements with the narrower capillary might be vitiated by errors due to surface tension. With the larger tubes the capillary effects are known and could be allowed for, since in all cases the height of the meniscus was determined. In most cases the correction thus introduced is very small. To ensure accuracy in the pressure gauge it was standardised against an open manometer. The difference of level in the pressure gauge and the tube containing MeF was found with an accurate cathetometer by swinging across on to a glass scale. This is the most difficult part of the measurements, but with a suitable instrument the difference of level can easily be found to

0·1 mm. The apparatus was tested with air, and found to give satisfactory values for the compressibility.

The MeF used was prepared from $KMeSO_4$ and KF. Two sets of determinations were made with different samples, the pressure gauge being in one case filled with air, and in the other with N. The compressibility data of Holborn and Otto (*loc. cit.*) were in each case taken as standard. The measurements were carried out at three different temps., 0°, 21°, and 44·5°. When pv was plotted against the corresponding value of p, the points in all cases lay on a straight line within the limit of error of our measurements. There is no evidence of curvature either positive or negative between pressures of 1 and 3 m. This is in general accordance with the equations of state of van der Waals and Beattie–Bridgeman, which indicate only very small curvatures for the conditions under which our determinations were made. We have accordingly assumed that the lines are straight, and calculated their equations by the method of least mean squares. The results are as follows, the pressures being expressed in m. of Hg, and the compressibility $1 + \lambda = p_0v_0/pv$ referring as usual to 1 atm.

$$\text{At } 0^\circ \left\{\begin{array}{ll} pv = 1 - 0{\cdot}01497p; & 1+\lambda = 1{\cdot}0115_1 \\ pv = 1 - 0{\cdot}01475p; & 1+\lambda = 1{\cdot}0113_4 \end{array}\right\} \text{Mean } 1{\cdot}0114$$

$$\text{At } 21^\circ \left\{\begin{array}{ll} pv = 1 - 0{\cdot}01152p; & 1+\lambda = 1{\cdot}0088_3 \\ pv = 1 - 0{\cdot}01115p; & 1+\lambda = 1{\cdot}0085_5 \end{array}\right\} \text{Mean } 1{\cdot}0087$$

$$\text{At } 44{\cdot}5^\circ \left\{\begin{array}{ll} pv = 1 - 0{\cdot}00923p; & 1+\lambda = 1{\cdot}0070_7 \\ pv = 1 - 0{\cdot}00898p; & 1+\lambda = 1{\cdot}0068_7 \end{array}\right\} \text{Mean } 1{\cdot}0070$$

Our preliminary measurements in narrow tubes also gave a value of 1·0114 for the compressibility at 0°. In order to indicate the accuracy of the method, typical exptl. results for each temp. are given below. The calc. results are those derived from the equations of the straight lines through the points.

	Press., m. of Hg.	pv, obs.	pv, calc.	pv, obs. — pv, calc.
At 0°	0·9466	0·98607	0·98604	+ 0·00003
	1·4981	0·97783	0·97791	− 0·00008
	1·9701	0·97126	0·97094	+ 0·00032
	2·5710	0·96223	0·96208	+ 0·00015
	2·8612	0·95736	0·95780	− 0·00044
At 21°	1·0239	0·98823	0·98822	+ 0·00001
	1·6109	0·98160	0·98146	+ 0·00014
	2·1127	0·97562	0·97569	− 0·00007
	2·6204	0·96947	0·96984	− 0·00037
	3·0601	0·96508	0·96478	+ 0·00030
At 44·5°	1·0788	0·99056	0·99032	+ 0·00024
	1·5425	0·98590	0·98615	− 0·00025
	2·0068	0·98192	0·98199	− 0·00007
	2·6016	0·97679	0·97665	+ 0·00014
	2·8900	0·97410	0·97406	+ 0·00004

Change of compressibility with temperature. According to the equations of state of van der Waals and Dieterici, the limiting value of the compressibility coeff. A_0 is given by

$$A_0 = \mathop{\mathcal{L}}_{p=0} \frac{1}{pv} \cdot \frac{d(pv)}{dp} = \left(b - \frac{a}{RT}\right)\frac{1}{RT}$$

in which b is the term involving the vol., and a that involving the attraction of the molecules in the two equations. Now, we have shown that for MeF, the slope of the pv–p curve is const. within the limit of error of our experiments between pressures of 1 and 3 m. For A_0 we may therefore write the experimental compressibility coeff. A, and we thus obtain

$$A = (b - a/RT)/RT.$$

Accordingly if AT is plotted against $1/T$ for various temps., a straight line should be obtained if b and a remain const. Actually the line is slightly curved in such a direction as to indicate that b increases with temp. Our experiments with other gases indicate that this curvature is not due to exptl. error, and moreover, it is in accordance with the observations of van der Waals. It may be noted, however, that, if it were assumed that the relationship between AT and $1/T$ is linear, the difference between the values of A obtained from the mean line and those measured experimentally would be small.

Theoretically according to the above equations of state, $A_c p_c$ = const., in which A_c is the compressibility at the crit. temp. and p_c is the crit. press. We are at present investigating various gases to see how closely this relationship holds.

Discussion of Results.

The results which we have obtained for the critical data show that these are the same within the limit of error of our experiments, whether the gas is made by Collie's method or from potassium methyl sulphate and potassium fluoride. The data are compared with those of Collie (*loc. cit.*) in the following table :

Critical constants of methyl fluoride.

Observer.	Critical temp.	Critical press., atm.	Critical vol., c.c./g.
Collie	44·9°	62	—
Authors	44·55	58·0 ± 0·2	3·33

There appears, therefore, to be no justification for the statement that pure methyl fluoride is not obtained by Collie's method or that there is any substantial error in his critical data.

Our value for the compressibility of methyl fluoride at 21°, *viz.*, 1·0087, is in satisfactory agreement with that determined by the microbalance, *viz.*, 1·0082, when account is taken of the fact that the latter measurements were only made over a pressure range of about 170 mm. At 0° our experimental value of the compressibility, 1·0114, also agrees well with the value which we calculated from our microbalance data at 21°, *viz.*, 1·0109. This result is somewhat higher than van Laar's calculated figure 1·0094 (" Zustandsgleichung," p. 46), but the difference is decreased by the new value for the critical pressure which we have found.

The Atomic Weight of Fluorine.—There still remains a large divergence between our figure for the compressibility at 0°, *viz.*, 1·0114, and that of Moles and Batuecas (*loc. cit.*), *viz.*, 1·018. There seems little doubt that our value is correct, since the two methods of measurement which we have used, although subject to entirely different errors, give substantially the same compressibility. If our compressibility at 0° be applied to the normal density of methyl fluoride determined by Moles and Batuecas, an atomic weight of fluorine of the order of 19·2 is obtained, instead of the value 18·998 which they found. It appears, therefore, that their determinations both of the normal density and of the compressibility of methyl fluoride are in error, and in consequence can scarcely be considered as evidence for the exact atomic weight of fluorine.

The most trustworthy data for this atomic weight appear to indicate that the chemical atomic weight is higher than that found by Aston for the 19 isotope, *viz.*, 18·995. Thus, the work of McAdam and Smith on the ratio NaF : NaCl, after their weighings had been corrected to a vacuum by Smith and Haagen, gave a value F = 19·009 (Carnegie Institution Report No. 267, p. 47). We have recalculated the reduction to a vacuum and confirmed their figure. Also the cross ratios obtained by Smith and Haagen (*loc. cit.*), in their work on the atomic weight of boron, gave an average value F = 19·005.

In deducing the molecular weight of methyl fluoride from our microbalance measurements, we extrapolated the pressure ratios of oxygen to methyl fluoride to zero pressure and thus obtained the limiting value of the ratio. By this procedure any errors in the experimental determinations of the ratios tend to be increased in the limiting ratio. A more accurate method of working is to apply our measured value of the compressibility of methyl fluoride to each of the ratios, and thus obtain a molecular weight of methyl fluoride independently from each ratio. To do this we make use of the formula

$$R = p_1/p_2 = (1 - A_1p_1)M_2/(1 - A_2p_2)M_1$$

in which R is the value of the ratio, A_1 and A_2 are the compressibility coefficients of oxygen and methyl fluoride at 21°, p_1 and p_2 the corresponding pressures expressed in atmospheres, and M_1 and M_2 the molecular weights. Now $A_1 = 0·00073$ approx. and $A_2 = 0·0086$. Making use of these compressibility coefficients in conjunction with our microbalance data given above, we obtain for the molecular weight of methyl fluoride from the two ratios the values 34·044 and 34·043, respectively. The mean value is 34·044, and assuming as before that the atomic weight of carbon is 12·010, we obtain for fluorine 19·011.

This value, when considered in conjunction with the measurements of McAdam and Smith, and of Smith and Haagen, *viz.*, 19·009 and 19·005, respectively, indicates that the atomic weight of fluorine lies between 19·005 and 19·010. If this is the case, fluorine must contain a higher isotope in appreciable quantity.

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