373. *The Molecular Weight and Limiting Density of Propane.*

By F. L. Casado, D. S. Massie, and R. Whytlaw-Gray.

Propane in a highly purified state has been prepared and its density compared with that of pure oxygen at 20·76° c. and at pressures of 700 and 350 mm. using a silica-fibre buoyancy microbalance.

The main object of the work was to see whether an exact value for the molecular weight of this gas could be obtained by a linear extrapolation of these ratios to zero pressure.

Although the *PV–P* isothermals at pressures below 1 atmosphere are for the permanent gases linear within very small limits; gases such as propane might be expected to show a slight curvature and if this were significant linear extrapolation would give too low a value for the limiting ratio and molecular weight. Actually the values found for the molecular weight of propane agree so closely with the figure from international atomic weights that it is concluded that any deviation from linearity is for this gas less than the errors of experiments. Direct compressibility measurements made at the same time support this view.

Adsorption which might affect the accuracy of the results has been measured and shown to have no appreciable effect on the final figure for the molecular weight which is 44·096.

Few determinations of high accuracy have been made in recent years of the limiting densities and molecular weights of so-called liquefiable gases, *i.e.*, gases which at room temperature are well below their critical temperatures. The most recent are those of Moles for ammonia, hydrogen sulphide, sulphur dioxide, and silicon tetrafluoride, for which he employed a very refined technique (*Trans. Faraday Soc.*, 1939, **35**, 1440; " Determination Physico-chimique des Poids Molec. et Atomique des Gaz," Collection Scientifique, Institut Internat. Co-operation Intellectuelle, Paris, 1938, pp. 1 and 74), and that for methyl ether carried out by Casado (Thesis, University of Santiago, 1943). In both, the densities were determined at a series of pressures from 1 to 0·25 atmosphere and were found to follow a straight line within close limits. For methyl ether Casado also made a series of direct compressibility determinations of from 1 atmosphere to about 200 mm. and obtained evidence of a strictly linear relation between *PV* and *P*. These and also the earlier experimental results of Cawood and Patterson (*J.*, 1933, 619) would seem to justify a straight-line extrapolation to zero pressure for liquefiable gases.

Moles's results have been criticised by Keesom on theoretical grounds (Determination Physico-chimique etc., p. 165), who calculates that the density–pressure graphs for the gases in question should shew a slight curvature towards the pressure axis and hence concludes that Moles's data should lead to slightly higher molecular weights.

The limiting-pressure method (Cawood and Patterson, *Phil. Trans.*, 1936, *A*, **236**, 77) and Whytlaw-Gray, Patterson, and Cawood (*Proc. Roy. Soc.*, 1931, *A*, **134**, 7) using a silica-fibre buoyancy microbalance has also been applied to the determination of the molecular weights of liquefiable gases, *i.e.*, xenon and hydrogen sulphide (see *ibid.*, p. 96), but, although the results obtained accord closely with the mass-spectrograph values, they are hardly accurate enough to throw much light on the question of curvature.

Although theory clearly indicates that at some temperature between the critical temperature and the boiling point a significant curvature in the low-pressure *PV–P* isothermals is to be expected, it has not so far been detected in any modern investigation, and all the evidence so far supports the contention of Moles that even for liquefiable gases at 0° c. a strictly linear extrapolation is applicable.

The object then of the present work was to determine accurately the molecular weight of propane by the limiting-pressure method, in order to see (*a*) of what degree of accuracy this method was capable and (*b*) whether the molecular weight so calculated exhibited any definite divergence from the true molecular weight which would indicate a slight curvature in the *PV–P* isothermal.

Experimental.

Microbalance.—The silica-fibre buoyancy microbalance used in this work is similar to the type described previously by Whytlaw-Gray, Patterson, and Cawood, and by Cawood and Patterson (*locc. cit.*). It was, however, of rather larger dimensions, carrying a suspended buoyancy bulb of 8·7 c.c., which reduced the ratio of surface to volume from 1 to 0·6. This buoyancy bulb was counterpoised at the other end of the 8-cm.-long beam by a smaller bulb with a hole in it, of very nearly the same weight, and the internal and external surfaces of which were together of approximately the same size as the external surface of the larger sealed bulb. By this means adsorption effects were compensated. Actually to get two bulbs of nearly equal weight and of such a size that their radii are in the ratio of $\sqrt{2} : 1$ was not easy. The bulbs were taken from a batch of small and large bulbs blown by Messrs. Cowlishaw and Co. of Manchester. The bulbs were measured and weighed, and a pair was selected which matched most closely.

Previously a flat plate had been used for surface compensation, but, since adsorption is apt to vary with the type of surface, it was thought that two blown bulbs offered a greater chance of equality. By measuring the finished balance it was estimated that the difference in surface moments computed from the geometric areas on either side of the fibre suspension was, at most, 10%.

The beam was constructed from 1-mm.-diameter vitreous-silica rod, slung between uprights on a transverse silica fibre. The uprights were carried by a silica framework made from 4-mm.-diameter rod, as shown in Fig. 1. The only operation in construction which presented difficulty and which has not been described before is the fixing of the fibre suspension. This was done as follows. The beam and its sealed-on adsorption bulb *BB*, and the supporting frame *AA*, having been made separately, the former was sealed to one of the frame uprights *CC* by a very thin silica rod, the frame itself being clamped in a vertical position (Fig. 2). A silica weight *D* was then sealed by a similar fine rod to the lower upright below the beam. The upper rod was next heated in the oxy-coal-gas blowpipe, being drawn out little by little into a fine fibre. During this process the beam was kept in position by resting on a double-pronged silica support *EE* which could be moved up or down by means of a delicate rackwork *G*. When the upper fibre had been drawn out to a suitable length and fineness, the lower rod was heated, drawn out into a fibre, and sealed to the lower frame upright. After removal of the pronged support, the balance and frame were next cautiously turned through a right angle to the horizontal position, and the hook and terminal fibre *H* for suspending the buoyancy bulbs were made by a similar procedure.

FIG. 1.

Microbalance.

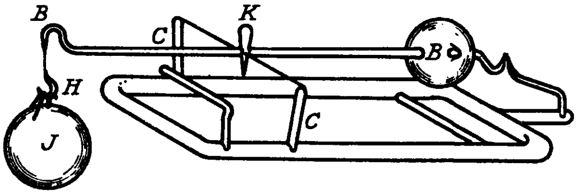
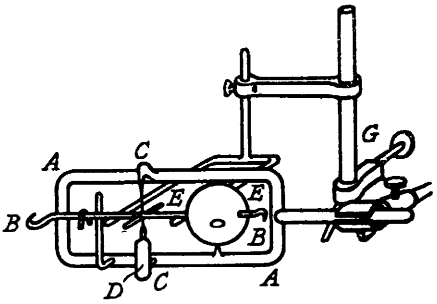


FIG. 2.



The balance was now ready for adjustment. It was placed under a bell jar after approximate equilibrium had been obtained by adding small weights to the buoyancy bulb hook. Then by altering the air pressure the beam was balanced to float, and its period of swing observed. By adding small amounts of silica to the piece *K* in the centre of the beam, or by removing small amounts from it, the centre of gravity could be raised or lowered until the period of swing indicated a suitable sensitivity. By raising the centre of gravity until the beam is just unstable and then volatilising small amounts of silica from *K*, it is possible, with a balance of the dimensions described, to get a period as slow as 50 seconds. It is better, however, to work with a lower sensitivity and a period of about 20 seconds.

Such a balance will easily detect a pressure change less than 0·01 mm. in air, and indeed throughout our work the balance was more sensitive than the pressure reading. When finally adjusted, it was heated in an electric furnace at 400° for some hours in dry and dust-free air and was then transferred to its glass case inside a thermostatted water-tank. The glass case was connected to the manometer and the rest of the apparatus through glass spirals which served to protect the balance from vibration and to prevent grease spray (from the taps) entering the case. The balance was approximately on the same level as the lower chamber of the manometer.

The limiting-pressure method has often been described, and it will be sufficient to say here that it consists in comparing the balancing pressures of the standard gas, oxygen, and some other gas, in this case propane, at two different densities. By the addition or removal of small weights from the suspended hook of the microbalance carrying the buoyancy bulb, the balance can be adjusted to float at any desired density. From the ratios so obtained the limiting ratio is calculated by linear extrapolation and the molecular weight obtained.

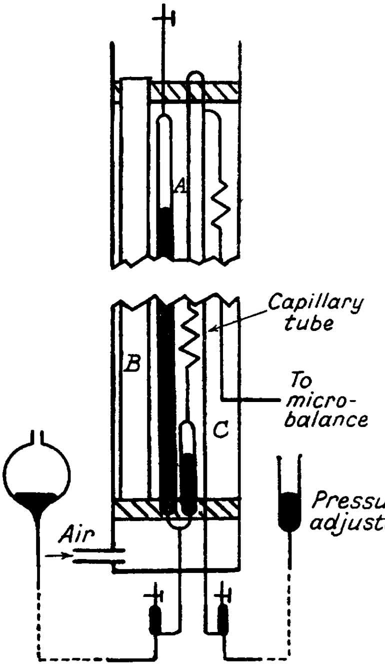
Since the main factor which limits accuracy, assuming adequate temperature control, is the pressure measurement, special care was taken to make the pressure readings as exact as possible.

Pressure.—The pressure was measured on a mercury manometer *A* (Fig. 3) contained in a thermostatted water-tank. Readings were taken by means of a cathetometer focussing on the mercury meniscus and then swinging through a small angle to focus on a Cowlishaw glass scale *B*, placed alongside the mercury column, in the water-tank. Moveable screens were arranged to slide behind the mercury column, touching the glass; and, by placing the screens so that only a small slit of light was visible between the meniscus and screen, errors due to reflection and refraction could be minimised and a clear image seen through the telescope. The two telescopes used were fitted with micrometer eyepieces so that the pressure could be read accurately to 0·01 mm. The manometer tube was constructed of 2·4-cm.-diameter tubing, to eliminate effects due to varying meniscus height (Whytlaw-Gray and Teich, *Trans. Faraday Soc.*, 1948, **44**, 774). Also on account of this, the pressure was always read with a rising meniscus in both limbs. As a fine adjustment to the pressure, the mercury in the capillary tube *C* could be raised or lowered.

Fig. 3 shows the manometer and connections. The fine tube above the lower limb of the manometer prevents the mercury, when raised suddenly, from flowing into the balance case. Glass spirals are included to reduce strain and vibrations.

The two tanks were thermostatted independently with the usual toluene regulator and electronic relay. The water was circulated in the tank containing the balance by a stirrer attached to a small motor. The temperature was read on a Beckmann thermometer the bulb of which was placed as close as possible to the balance case. It remainded constant within 0·005° over the period of a reading. Another thermometer in a different part of the bath was used as a check on the adequacy of the stirring. The stirring of the manometer tank presented greater difficulty, as a very long spindled stirrer was necessary to reach the bottom of the tank. The vibrations set up by this arrangement were found seriously to affect the setting of the balance. Eventually it was found that adequate stirring could be obtained by a continuous blast of air, from the compressed-air supply, blown through a pipe let into the base of the tank. The temperature was read on an ordinary mercury thermometer to 0·01°.

Fig. 3.



The two tanks containing the manometer and the microbalance were erected on a stone table in a basement room, so as to avoid vibration as far as possible. The micro-balance tank was further protected by resting on thick rubber bungs.

Care was taken to avoid, as far as practicable, unjacketted connections outside the tanks. As finally arranged, the manometer was connected to the balance case by an 8-cm.-long glass tube of 2-mm. bore outside the tanks, and this was lagged with cotton wool.

The temperatures in the tanks were very nearly equal, that of the balance tank being on an average 20·76°, and that of the manometer 20·90°.

Preparation of the Gases.—(a) *Propane.* Initially the propane was obtained from a cylinder supplied by I.C.I. as 98—99% pure. This gas contained up to 1·5% of butane and up to 0·5% of ethane. We found that it also contained unsaturated hydrocarbons, mainly propylene and possibly *cyclo*propane.

We are indebted to Dr. Atack and Dr. McCormack, who were using the gas in quantity for their own researches in this Department, for kindly carrying out for us a preliminary fractionation and for supplying us with a middle fraction which formed our starting material.

This sample was then subjected to chemical treatment and finally further fractionation, since the boiling points of propylene (−47°) and propane (−44·5°) lie so close together. The gas was first passed through conc. potassium permanganate solution made slightly alkaline, contained in a tower and U-tube filled with glass beads, for the removal of the unsaturated compounds. It was then dried by a soda-lime tube and passed through a second tower containing fuming sulphuric acid, and two U-tubes containing concentrated sulphuric acid activated with silver sulphate as a catalyst. The gas was finally dried (P_2O_5), and about 40 c.c. were condensed in a vessel surrounded with liquid air. About a third of this liquid was allowed to evaporate and was rejected. The second fraction was condensed at the foot of a fractionating column, and the remaining fraction also rejected. In this way the lighter impurities such as ethane (b.p. −88°), and heavier compounds such as butane (b.p. −0·6°), were mostly eliminated.

The fractionating column, about 20 cm. long, contained a copper spiral and was constructed after the method of Booth and Swinehardt (*J. Amer. Chem. Soc.*, 1935, **57**, 1934). The top of the column was cooled with a mixture of solid carbon dioxide and alcohol. When the liquid was refluxing vigorously and a steady state had been reached, small fractions of gas were taken off so as to maintain a steady pressure of about 350 mm. in the gauge. The various fractions were subsequently stored in evacuated bulbs.

The balancing pressures of the various fractions were then determined with the microbalance. A very large number of determinations was made, and the results were compared as a test of purity. When agreement was not sufficiently good, the gas was refractionated, rejecting the first and last fractions, until the balancing pressures of the middle fractions were identical. This sample of gas was finally regarded as pure and was used for the first series of accurate comparisons with oxygen at two different pressures.

The obtaining of this pure propane formed one of the most difficult parts of the work, involving much labour and patience in the testing and refractionation of the various samples. [At this stage it was thought that vapour pressure measurements at the temperature of solid carbon dioxide and alcohol might furnish a further test of the purity of the gas. A number of measurements with different samples was made, but this method proved less sensitive than a comparison of balancing pressures. We found 105·8 mm. as the vapour pressure at −78·5°, which is lower than the value 130·5 mm. from the vapour-pressure measurement of Burrel and Robertson (*J. Amer. Chem. Soc.*, 1915, **37**, 2188).] The ratios obtained from this first series were not very consistent. This might have been due to impurities still remaining in the gas, most probably traces of unsaturated compounds, and it was decided to hydrogenate the gas and then purify it as before. Dr. Atack and Dr. McCormack kindly hydrogenated a sample of their original gas, over a promoted nickel catalyst at 300—350°. The resulting gas was condensed in a vessel surrounded with liquid air. One third was allowed to boil off, removing most of the ethane. The second fraction, about 4 l. of gas, was transferred to evacuated storage flasks. The remaining third of the liquid was discarded, containing most of the heavier impurity butane. The hydrogenated gas was subjected to the same chemical purification as before except that it was passed and repassed through the purification train five times in all. It was then fractionated as previously and collected in two fractions. The third fraction was rejected.

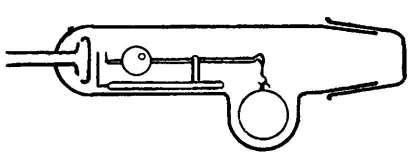
A second series of accurate comparisons with oxygen at two different pressures was obtained from the second fraction of this sample of propane. The results obtained were more consistent than those of the first series. The final calculation of the molecular weight of propane showed very good agreement between the two series, suggesting that gas of a very high standard of purity had been obtained.

Earlier, an attempt had been made to prepare propane from propyl cyanide and sodium by Timmermans's method (*J. Chim. physique*, 1920, **18**, 133). Only a small quantity of gas was obtained, insufficient for a series of experiments. On testing with the microbalance it was found to be too light, probably owing to the presence of unsaturated hydrocarbons. This method of preparation was therefore abandoned and the more profitable one detailed above used.

(b) *Oxygen.* The oxygen used as the standard for the comparisons was obtained from "AnalaR" potassium permanganate. Initially, air was expelled by evacuating, then heating slightly, and evacuating again. The oxygen was passed over solid potassium hydroxide to eliminate possible traces of carbon dioxide and then dried (P_2O_5). It was next bubbled through mercury to remove traces of ozone, and finally taken into the balance case through a long glass spiral cooled in liquid air. The oxygen was freshly prepared for each filling, and not stored.

Course of an Experiment.—Before making a filling with either gas, the whole apparatus was thoroughly evacuated. A Speedivac oil-pump was used until the pressure was about 0·002 mm., and the remaining traces of gas were removed with a charcoal tube cooled in liquid air. The pressure was tested by means of an accurate McLeod gauge until it registered practically zero. It was usually possible, with the charcoal tube, to reach a pressure of about 0·00008 mm. in about 20 minutes. It was necessary to leave the apparatus in a high vacuum overnight and then pump down again before interchanging the gases. If this was not done, particularly when the previous gas in the apparatus was propane, the pressure readings on the second gas showed a decided drift, presumably owing to slow release of gas adsorbed by the greased joints and the glass walls. This long period of high vacuum was more satisfactory in removing adsorbed gases than washing out with the gas before filling.

FIG. 4.



To obviate this adsorption, an alternative to Apiezon grease was sought. Finally, the original soda-glass balance case with two ground joints was replaced with a Pyrex case with one joint (Fig. 4). Also the connecting tubes were modified to reduce the number of taps. Edwards W.E.Wax No. 6 proved the most satisfactory for the balance-case joint, having little or no vapour pressure at 20° and being unaffected by the gases used. When the second series of propane measurements was made, these modifications to the apparatus helped to eliminate the delayed desorption of propane, and the lowering of the oxygen pressure was not so noticeable.

To ensure that the propane was free from air before taking it into the balance case it was liquefied in a small bulb immersed in liquid air, which was close to the balance case, and then thoroughly evacuated first with the Speedivac pump and finally with the cooled charcoal tube. The pressure was tested on the McLeod gauge and could easily be lowered to 0·0001 mm. The liquid was then allowed to evaporate and the gas taken into the balance case and manometer very slowly until the balance began to swing freely. The balance was adjusted roughly by means of the main mercury reservoir so that the fixed pointer and the pointer attached to the balance were in a horizontal line. The points were viewed through a telescope with a micrometer eyepiece through a glass window in the side of the tank.

Before making the final adjustment, the tube connecting the mercury reservoir to the manometer (Fig. 3) was clipped to prevent alterations in the barometric pressure from affecting the reading. The final adjustment was made with the pressure adjuster. After filling, it was necessary to leave the apparatus for 3—4 hours for steady temperature conditions to be reached. The balance was then set accurately to the zero point, and the pressure read off on the manometer, each reading being taken three times, and the mean determined. The temperatures of the balance case and manometer tank were noted. After about an interval of an hour, the mercury in the manometer was lowered by a few mm. by means of the main reservoir and then raised again. The balance was reset, and the pressure and temperatures recorded a second time. About five sets of readings were taken in this manner.

After evacuation of the apparatus as described above, the freshly prepared oxygen was taken into the apparatus to the approximate balancing pressure and readings taken as for propane.

Table I shows a typical series of results for two consecutive fillings of propane and oxygen, respectively, taken from Series II.

Corrections.—Various corrections have to be applied to the results before the final figure is obtained. The thermometers used in the manometer tank and tank surrounding the balance case were compared with an N.P.L. Standard thermometer of 20—30° range, and a list of corrections drawn up to 0·01°.

The glass Cowlishaw scale used to measure the pressure was compared with a Standard Société Genevoise Scale, and a correction curve drawn.

The mercury column was corrected to 0°, latitude Leeds. The balance-case temperature was corrected in each case to 20·76°, that being the mean temperature of the experiments. It was not considered advisable to carry out the necessarily large extrapolation involved in reducing all balancing temperatures to zero.

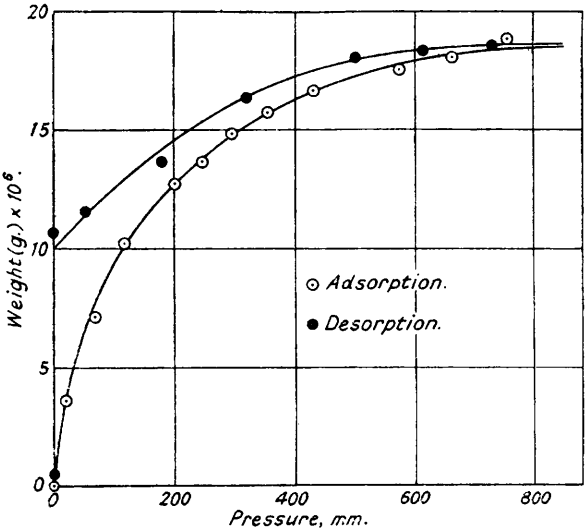
Finally a Rayleigh correction was made for change of buoyancy due to the slight contraction when propane is replaced by oxygen. The contraction of the bulb, measured on a bulb of similar volume and weight, was found to be 3 cu. mm. per 760 mm. pressure.

Results.—Propane and oxygen were put into the balance case, alternately. Several readings were

TABLE I.

Corrected scale readings.		Pressure, mm., Hg.	Corrected manometer temp., °c.	Corrected balance temp., °c.	Pressure, corrected to 0° c., mm.	Pressure, corrected to balance temp., 20·76°, mm.	Mean pressure, mm.	Final pressure, mm. Buoyancy correction added.
444·47	947·33	502·86	20·90	20·764	501·05	501·05		
444·26	947·14	502·88	20·91	20·766	501·07	501·05		
444·11	946·99	502·88	20·90	20·761	501·07	501·07	501·06	501·12
444·16	947·04	502·88	20·90	20·766	501·07	501·05		
444·23	947·10	502·87	20·90	20·759	501·06	501·06		
225·90	926·33	700·43	20·92	20·771	697·92	697·90		
225·83	926·27	700·44	20·92	20·759	697·93	697·93		
225·72	926·18	700·46	20·92	20·763	697·95	697·95	697·92	697·94
225·90	926·36	700·46	20·91	20·769	697·95	697·93		
225·88	926·32	700·44	20·91	20·769	697·93	697·91		

FIG. 5.



Weight of propane adsorbed on surface of 123 *sq. cm. for pressure range* 0—800 *mm.*

taken with each filling, taking about a day and a half. Individual measurements agreed within 0·03 mm. The results, recorded in Tables II and III, are a summary of all the measurements taken, after all corrections have been applied. Each pressure reading is the mean of about five readings. The measurements in each series were consecutive. All the results obtained are included.

Adsorption.—To find out to what extent this effect could impair the accuracy of our results, the adsorption of propane on blown surfaces of vitreous silica was measured independently by direct weighing, using another microbalance designed for this purpose. In Fig. 5, the total weight adsorbed is plotted against pressure.

From these results the weights of propane adsorbed on the surface of the buoyancy bulb were calculated, for pressures of 501 and 254 mm., as $2{\cdot}8 \times 10^{-6}$ g. and $2{\cdot}3 \times 10^{-6}$ g., respectively. These figures would give a correction to the observed balancing pressures of 0·13 and 0·11 mm., which would increase the molecular weight from 44·098 to 44·124, corresponding to an increase in the atomic weight of carbon from 12·011 to 12·020. Hence had the balance been uncompensated the results obtained would have been too high by this amount. Actually, since the surface areas on the two sides of the balance beam were within 10% of equality, we regard our results as free from adsorption error within the limits of accuracy of our measurements.

The work mentioned on the adsorption of propane has not yet been published. The values obtained seem to us very large in comparison with corresponding concordant values obtained with sulphur dioxide in two investigations in this laboratory. It seems unlikely that the adsorption of propane on blown-silica surfaces is so much greater than that of sulphur dioxide. Although great care was taken to ensure clean surfaces, it is possible that these were contaminated by adsorbed Apiezon-grease vapour from the ground joints in the adsorption-balance case and that the values obtained are for adsorption on a grease film. Since, however, the density balance was equally liable to grease-vapour contamination in the first series, we have used the high values in the above calculation to obtain a measure of the maximum possible error.

TABLE II.

Series I.

	Low pressure. Mean corrected pressure, mm. Hg.		Ratio	High pressure. Mean corrected pressure, mm. Hg.		Ratio
	O_2	C_3H_8	O_2/C_3H_8.	O_2	C_3H_8	O_2/C_3H_8.
	352·58	—	1·38538	—	478·95	1·39165
	—	254·50	1·38534	666·53	—	1·39165
	352·57	—	1·38534	—	478·95	1·39167
	—	254·50	1·38503	666·54	—	1·39208
	352·49	—	1·38492	—	478·81	1·39170
	—	254·52		666·36	—	1·39150
				—	478·88	1·39137
				666·30	—	
Mean values :	352·540	254·504	1·38520 ±0·00008	666·451	478·890	1·39166 ±0·00005

Cawood and Patterson (*loc. cit.*) derived the expression

$$p_1/p_2 = [M_2(1 - A_1p_1)]/[M_1(1 - A_2p_2)] = r$$

where r is the ratio of the two pressures, and A is the compressibility as defined by $p_1V_1/p_0V_0 = 1 - A$.

This gives a linear plot of r against p, and, extrapolating to zero pressure, we have limiting ratio, $r_0 = M_2/M_1$.

Since M_1 = molecular weight of oxygen = 32, r_0 = 1·37794, the molecular weight of C_3H_8 = 44·094. Assuming H = 1·0080, the atomic weight of carbon = 12·010.

TABLE III.

Series II.

	Low pressure. Mean corrected pressure, mm. Hg.		Ratio	High pressure. Mean corrected pressure, mm. Hg.		Ratio
	O_2	C_3H_8	O_2/C_3H_8.	O_2	C_3H_8	O_2/C_3H_8.
	—	254·49	1·38540	697·95	—	1·39275
	352·57	—	1·38551	—	501·13	1·39273
	—	254·47	1·38543	697·94	—	1·39276
	352·55	—	1·38548	—	501·12	1·39276
	—	254·46	1·38560	697·94	—	1·39243
	352·58	—	1·38533	—	501·24	1·39265
	—	254·51	1·38537	698·05	—	1·39267
	352·59	—		—	501·23	
Mean values :	352·570	254·481	1·38545 ±0·00002	697·973	501·173	1·39268 ±0·00002

Limiting ratio, r_0, = 1·37807 ± 0·00006.
Molecular weight of C_3H_8 = 44·098 ± 0·002.
Assuming H = 1·0080, the atomic weight of carbon = 12·011 ± 0·001.

DISCUSSION.

From the results obtained in the two series of measurements it is evident that a linear extrapolation to zero pressure, *i.e.*, extrapolation over a range of 352 mm. of oxygen pressure gives two values (44·094 and 44·098 ± 0·002) for the molecular weight of propane which are in close accord and differ only slightly from the molecular weight calculated from International atomic weight values, *i.e.*, 44·094.

In view of the slight uncertainty in the third decimal place of the atomic weight of carbon, due to a variation in the C_{12}/C_{13} ratio in carbon from different sources (Nier, *J. Amer. Chem. Soc.*, 1939, **61**, 697), the agreement of our results (12·010 and 12·011 ± 0·001) with the standard is as close as can be hoped for.

It is thus concluded that a strictly linear extrapolation is, for this gas, fully justified and that any curvature in the *PV–P* isothermal at 20·76° for propane, a gas with a critical temperature of 95°, is beyond the limits of accuracy of our measurements.

Strong support for this conclusion is afforded by an independent research on the compressibility of propane carried out in these laboratories by Dr. G. A. Bottomley. A full account of this work will be published shortly, and only his final results will be quoted. Using a specially-designed differential-compressibility apparatus (Thesis, Leeds, 1946), which by measurements with nitrogen and carbon monoxide was proved to give high accuracy, he determined the *PV–P* isothermal for propane at 22·02° from 800 to 100 mm. pressure. Two sets of measurements were made of 6 and 5 points, respectively. Strict mathematical treatment by the method of least squares showed the deviation from a straight line to be indetectable and within the limits of the errors of experiment.

The mean value found by Dr. Bottomley for the coefficient of deviation from Boyle's law for propane at 22·02° is $A_{C_3H_8}$ = 0·016814 per atmosphere.

To correct the value from 22·02° to 20·76°, the temperature at which the microbalance ratios were measured, a small correction is necessary. We have used for this correction the values found for A for propane at 0° and 50° by Jessen and Lightfoot (*Ind. Eng. Chem.*, 1938, **30**, 312) and interpolated these assuming a linear relation between A and $1/T$. The corrected value for 20·76° then becomes 0·016991.

Using the same apparatus we have determined the corresponding coefficient for oxygen at 22·02° as A_{O_2} = 0·00068 per atmosphere. Using this latter coefficient we can calculate from our micro-balance ratios the compressibility coefficient of propane by means of the formula (Cawood and Patterson, *loc. cit.*, p. 99),

$$A = \frac{r''(1 - A_1p_1') - r'(1 - A_1p_1'')}{r''(1 - A_1p_1')p_2'' - r'(1 - A_1p_1'')p_2'}$$

where r' and r'' are microbalance ratios, p_1' and p_1'' are oxygen pressures, p_2' and p_2'' are corresponding propane pressures, and A_1 is the compressibility of oxygen.

Thus, we find for Series I, A = 0·016584, and for Series II, A = 0·016832. Series II, which we regard as the soundest experimentally, gives a value for the compressibility which agrees satisfactorily with the above value found by Dr. Bottomley. Series I gives a distinctly lower value and exemplifies what has been noticed before, that microbalance ratios when extrapolated to zero pressure may give a correct limiting value, but an incorrect slope (Patterson and Cawood, *loc. cit.*, p. 100).

Using Dr. Bottomley's corrected value for the compressibility and our value for oxygen, we can now calculate values for the molecular weight of propane from each pressure ratio in Series II (Table III) from the expression on p. 1751. These are low-pressure ratio 44·096, high-pressure ratio 44·094, and mean 44·095. We have then, for the molecular weight of propane, the following :

	Mol. wt.	At. wt. of carbon (H = 1·0080).
Microbalance, series I	44·094	12·010
,, ,, II	44·098	12·011
Compressibility, series II	44·095	12·010
Mean	44·095 (7)	12·010 (6) *

* Calc. from mean mol. wt.

These figures appear to us to be the most probable from our data.

We wish to express our thanks to the Department of Scientific and Industrial Research for an assistantship to one of us (F. L. C.) and to Imperial Chemical Industries Ltd. for the help of another (D. S. M.). The third author thanks the Leverhulme Trustees for financial support during the earlier part of the work. One of us (F. L. C.) also thanks the Patronato de la Universidad de Santiago de Compostela for a scholarship covering the earlier part of the work.

THE UNIVERSITY, LEEDS.

[*Received, December* 15*th*, 1948.]