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LIMITING DENSITIES AND MOLECULAR WEIGHTS OF OXYGEN; CARBON DIOXIDE, SULPHUR DIOXIDE AND HYDROGEN SULPHIDE.—ATOMIC WEIGHTS FOR CARBON AND SULPHUR.

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If the weights of equal volumes of a gas and of oxygen at 0° and under different pressures between 0 and 1 atmosphere are determined and the obtained values referred to the normal value of p and are put into two series :—

$$L_{p}, L_{p}^{\circ}, L_{p}^{\circ}, \ldots, L_{\lim}^{\circ}$$

 $L_{p}^{\circ}, L_{p}^{\circ}, L_{p}^{\circ}, \ldots, L_{\lim}^{\circ}$

we can, by linear extrapolation to zero pressure, obtain the limiting densities and therefore the density of the gas under ideal (Avogadro's) conditions.

Since the gas laws are only exact at indefinitely low pressures, the application of Avogadro's principle that the molecular weights of gases are proportional to their densities, *i.e.*,

$$\frac{M}{d}, \frac{M'}{d'}, \frac{M''}{d''}, \dots$$
 const.

is only strictly true when the limiting densities L_{lim} , L_{lim} , L'_{lim} are employed in the calculation. Hence, if we take in the above system of proportional numbers M = 32,000 (conventional molecular weight for oxygen), $M' = 32,000 L'_{\text{lim}}/L_{\text{lim}}$ is the most simple and logical expression for Berthelot's rule of the limiting densities.¹ We can take also the relative values of density as density ratios $r, r', r'' \ldots$, from which the limiting ratio r_0 for p = 0 can be extrapolated. Consequently $M' = 32,000 \times r_0$.

The best method of extrapolating experimental results in order to obtain the limiting densities is still under discussion. From van der

¹ C.R. Acad. Sci., 1898, 126, 954.

Waals' equation and other theoretical considerations, the relationship between compressibility and, therefore, between normal density and pressure should be represented as a function of the second degree $L_p = a + bp - cp^2$. For the less compressible gases the p^2 term can be neglected.

It has recently been shown² that for all gases, including the exceedingly compressible ones, the relationship between L_p and p is certainly strictly linear over the pressure range between 0 and 1 atmosphere for which Berthelot's rule applies and within the limit of error (10^{-5}) of our experiments. No difference is noticed between less and more compressible gases when values are used which have been corrected for adsorption.

It has been shown³ that the determination of molecular and atomic weights within an accuracy of 10⁻⁴ requires a knowledge of density values and therefore of all related data (pressure, temperature; weight of gas) to at least 10⁻⁵. This degree of accuracy may be easily obtained by following the improved technique which has been fully described elsewhere.^{3,4} In previous work we recommended, on account of practical limitations, that measurements should be taken over the range between 0.5 and I atmosphere. In this paper a full account is given of recent experiments with compressible gases over the range between 0.25 and 1.0 atmosphere, in which the precision has been kept within 10^{-5} . This enables extrapolation to the limiting densities to be made with greater accuracy.

Apparatus.

Density was measured with the volumeter by the displacement as well as by the condensation method. Two different volumeters A and B were used, both of which comprised two independent flasks of about 2400 ml., each of which could be filled either together or separately, with a known weight of gas, thus giving two different values of density. Volumeter A had previously served for determining the density of ammonia. It was made entirely of Thuringian glass and served in the present research for density measurements on oxygen (I), ethylene and sulphur dioxide. The final apparatus is shown diagrammatically in Fig. 1. Volumeter B, of the same size, was used for measuring the limiting densities of oxygen. (II), carbon dioxide and sulphur dioxide (II). It was used originally to measure the correction for adsorption. The measuring system (bulbs V, V', barometer B, weighing apparatus C and connecting tubes) was made wholly of Jena glass which adsorbs three or four times less than Thuringian glass.⁵ The whole measuring system together with the mercury reservoir R was kept at o° C. in ice to avoid any correction for temperature. Raising or lowering the mercury in the barometer was effected by letting in or removing dry pure air through tap t. Thus mercury never came in contact with greased taps or rubber tubing. The setting of the mercury to the fixed pointer p in the shorter line of the barometer was always made -with a rising meniscus. This meniscus always remained very clean.

² E. Moles and T. Toral, Monatsh., 1936, 69, 342; Anal. Fis. Quim., 1937, ² E. Moles and I. 10ral, Monatsh., 1930, 09, 342; Anal. Fis. Guim., 1937, 35, 42; E. Moles, J. Chim. physique, 1937, 34, 19; Anal. Fis. Guim., 1937, 35, 134; E. Moles and T. Toral, Z. anorg. allg. Chem., 1938, 236, 225; E. Moles, Arch. Sci. phys. nat. (5) 1938, 20, 59; E. Moles, Les determinations physico-chimiques des poids moleculaires et atomiques des gaz (Inst. int. Cooperat. int., 1938, Paris); E. Moles, Bull. Soc. chim. Belgique, 1938, 47, 405.
^a E. Moles and T. Toral, Z. anorg. allg. Chem., 1938, 236, 225.
⁴ E. Moles and T. Toral, Monatsh., 1936, 69, 342.
⁵ M. Crespi and V. Aleixandre, Anal. Fis. Quim., 1934, 32, 931; 1936, 34, 315.

We give the following characteristics of the volumeter :

Volumeter A.	v = Volume.	w = Weight.	Contraction per 1 atm.
Bulb I	2559·56 ml.	219·2 g.	- 0.465 ml.
,, II	2381·09 ,,	246·1 "	- 0.360 ,,
Bulb. J_1	2273·14 ,,	350 · 0 ,,	-0.230 ,,
	2270·86 ,,	322·5 ,,	-0.240 ,,

to which the volume of the connecting tubes and of the dead space in the shorter line of the barometer must be added to obtain the total volume. The contraction of the bulb between the different pressures was calculated



after the formula of Moles and Miravalles, ⁶ viz., $c = v/w \times 15.5 \times 10^{-5}$ ml. The following figures show an example of the changes of this correction :—

Pressure	1.00000	0.750000	0.66667	0.20000	0.33333	0.250000 atm.
Bulb I. 🛛	2559.56	2559.45	2559.40	2559.33	2559.25	2559·20 ml.

Changes due to breakage and subsequent repair of the apparatus proved to be negligible.

Pressures.

Observations were made with a reading microscope to ± 0.01 mm. on glass scales mounted in front of the barometer. Scale A requires a correction of length of $\pm 199 \times 10^{-6}$ mm. per mm. and has the expansion coefficient $\beta 9.3 \times 10^{-6}$, scale B requires correction of $\pm 381 \times 10^{-7}$ mm. per mm. and $\beta = 9.2 \times 10^{-6}$ as measured in the precision comparator. To refer the measured pressures to 45° latitude and sea level, we used the factor 0.999323 experimentally determined in our Institute. As has been said, readings were always made *par ascensum*, which gives a very clean meniscus and in every case the heights of the upper and of lower

⁶ J. Chim. physique, 1924, 21, 1.

meniscus were the same within ± 0.001 mm., so that no correction is required. For example :—

Pressure .	.	1.0000	0.75000	0.6250	0.50000 atm.
Upper meniscus	•	0.901	0.904	0.903	0•907 mm.
Lower ,,	- 1	0.902	0.904	0.902	0.905 ,,

Temperature.

The limiting densities method requires that both the examined gas and oxygen be kept at the same temperature near o° C. It is very important to ensure the constancy of this temperature, rather than its exact value. We find that constancy within \pm o·oor° is easily obtained by using common ice washed with distilled water. We give a series of readings on the Beckmann thermometer as an example: 5.229°, 5.227°, 5.227°, 5.229°, 5.228°, 5.228°, mean 5.228°. Using pure ice manufactured by us with distilled water 5.228° was read.

Weighing of the Gases.

Gases were weighed by double weighing and employing a counterpoise on a precision balance with the sensibility \pm 0.01 mg. with a load of 200 g. By the displacement method (e.g., for oxygen) the weight of evolved gas



is determined by difference in the weight of the gas generator before and after heating. A model of the gas generator before and after heating. A model of the gas generator is given in Fig. 2. In the condensation method (CO₂, C_2H_4 , SO₂) the gas was always condensed in weighing tubes (see Fig. 1) charged with about 20 g. activated charcoal which had been previously dried and purified by heating it to 200° *in vacuo*, washing out several times with pure gas and pumping off. The gas

times with pure gas and pumping off. The gas condenser was cooled in liquid air. Desorption took place very easily and desorbed gas was recondensed many times and used again and, since it always showed identical density, was very pure.

Preparation of Gases.

The individual gases were prepared as follows :---

Oxygen.—Purest recrystallised KMnO₄ charged in a gas generator was heated to 250° in vacuo. The evolved gas was passed over solid KOH through a drop of mercury and dried over P₂O₅, all contained in the gas generator (Fig. 2). The purity of the oxygen was ascertained by comparing the density of the different samples.

Ethylene was prepared by the dehydration of pure ethyl alcohol over activated Al_2O_3 (obtained by heating $Al(NO_3)_3$ to $350^\circ-400^\circ$) heated to 350° C. The evolved gas was passed through a condenser immersed in Thilorier mixture (solid CO_2 + acetone), washed in acidified solution of FeSO₄ and dried over conc. H_2SO_4 and P_2O_5 .

Another sample of ethylene was prepared by heating on a sand bath to $200^{\circ}-220^{\circ}$ a mixture of 75 p. of metaphosphoric acid (after Moissan) with 25 p. alcohol to which was added with some P₂O₅ and sand. It was purified by cooling to -80° in Thilorier mixture, washed through 50 per cent. KOH solution and then dried, liquefied and fractionated.

Carbon dioxide.—One sample of this gas was prepared by heating to 95° -100° C. in a vacuum purest recrystallised Na₂CO₃ dried previously at 70° C. The evolved gas was cooled in a mixture of common salt and ice, dried over H₂SO₄ and P₂O₅ and then condensed and sublimed.

Another sample was obtained by heating to $360^{\circ}-380^{\circ}$ C. pure dried MgCO₃ and then purifying it in a similar manner.

Sulphur dioxide.—Compressed SO_2 gas from a cylinder was dried over conc. H_2SO_4 and P_2O_5 , then condensed and frationated.

Another sample was prepared by the action of hot concentrated H_2SO_4 on mercury in a high vacuum and purified as above.

The gas reacts also with tap grease under the influence of light. It was necessary, therefore, to work in diffused light and to surround the storage flasks with black paper.

All gases were repeatedly filtered through Schott's sintered glass filters. With the exception of CO_2 the gases were all bubbled through a little liquefied gas. The non-fouling of the mercury in the barometer over long periods of time is attributed to these precautions, so that exceedingly reliable readings were obtained.

Results.

The results are shown in Tables I and II where P_0 is the corrected pressure referred to normal conditions, s is the weight of gas, L_p the gross weight of a litre and L_0 the corrected weight of a litre. As a most convenient practice, some corrections were directly done on the L_0 values. Thus the vacuum reduction was made by the formula $v = \frac{L_0}{8\cdot 4} \times 0.0013$. The compressibility coefficients per mm. deduced from our measurements were as follows: O_2 , $I\cdot7 \times I0^{-6}$; CO_2 , $I\cdot8 \times I0^{-5}$; C_2H_4 , $I\cdot19 \times I0^{-5}$; SO_2 , 9.01×10^{-5} ; SH_2 , $2\cdot38 \times I0^{-5}$.

The numbers in Table I (1, 3, 4 and 5) were due to Moles and Roquero and determined in 1935; those in Table I (2 and 6) were obtained recently by Moles and (Miss) Toral in the same apparatus. The agreement between all the series is as good as possible and proves the inalterability of the apparatus.

TABLE I.—THURINGIAN GLASS.

	Expt. No.	P ₀ .	υ.	s.	L_{p} .	L ₀ .
1.	Oxygen	under 76	0 mm.		-	
	Ι	760.370	2564·19 ml.	3.66643	1.42916	1.42895
	II	745.559	2564.19	3.59505	1.42917	1.42898
	III	766.160	2392.72	3.44734	1.42917	1.42895
	IV	755.575	2564.19	3.64327	1.42914	1.42894
	\mathbf{v}	756.580	2564.19	3.64804	1.42912	1.42892
					mean .	$ \frac{1.42894_{8}}{\pm 0.000010} $
2.	Oxygen	under 57	0 mm.			
	I	573.83	2393.51	2.58204	1.42876	1.42856
	II	571.34	2393.51	2.57092	1.42880	1.42860
	III	570.80	2393.51	2.56857	1.42884	1.42864
	IV	570.01	2393.51	2.56491	1.42879	1.42859
					mean .	. 1·428597 ± 0·00001 ₆
3.	Oxygen	under 50	6 mm.			
	Ι	509.680	2564.04	2.45685	1.42878	1.42856
	11	502.348	2564.04	2.42146	1.42876	1.42855
	111	514.712	2564.04	2.48085	1.42863	1.42840
	IV	509.950	2564.04	2.45809	1.42876	1.42854
					mean .	$. 1.42851_{2}$ ± 0.00002

TABLE I.—THURINGIAN GLASS.—Continued.

	Expt. No.	P ₀ .	v.	s.	L _p .		L _e .
4.	Oxygen	under 3	80·00 mm.				
	I	393.908	495 ^{1.8} 7	3.66643	1.42853		1.42829
	_11	386-245	4951.87	3.29202	1.42852		1.42829
	111	370.397	4951.87	3.44734	1.42843		1.42828
	11	391.420	4951.87	3.04327	1.42854		1.42830
	V	391.945	4951.87	3.04804	1.42850		1.42826
					mean .		1.428284
_	. .					±	0.000006
5.	Oxygen	under 2	53·33 mm.				
	I	263.995	4951.74	2.45685	1.42836		1.42810
	11	260.210	4951.74	2.42146	1.42826		1.42802
	111	266.591	4951.74	2.48085	1.42827		1.42800
	IV	264 • 1 3 5	4951.74	2.45809	1.42832		1.42806
					mean .		1.42804-
						±	0.00001
6.	Oxygen	under 1	90 mm.				
	I	192.08	4951.86	1.78747	1 42824		1.42802
	II	193.13	2392.64	o·86832	1.42811		1.42789
	III	190.36	4951.86	1.77149	1.42824		1.42802
	IV	206.41	2392.64	0.92806	1.42817		1.42792
	v	190.24	2393.33	0.85565	1.42823		1.42801
	VI	193.22	2393.33	0.87033	1.42814		1.42792
					mean .		1.42796.
						±	0.00002
7.	Ethylen	e under	760 mm.				
	I	740.92	2392.97	2.94023	1.26034		1.26037
	II	746.88	2392.97	2.96401	1.26039		1.26035
	III	762.22	2392.97	3.02549	1·26064		1.26041
	IV	764.83	2392.97	3.03573	1.26058		1.26033
	v	754.90	2392.97	2.99610	1.26048		1.26033
	VI	674.14	2392.97	2.67359	1.25956		1.26036
					mean .		1.26035.
						±	0.00001
8.	Ethylen	e under	570 mm.*				
	I	569.05	2392.82	2.25433	1.25826		1.25807
	II	573.21	2392.82	2.27096	1.25833		1.25809
	III	547.94	2392.82	2.17035	1.25804		1.25810
	IV	576.71	2392.82	2.28488	1.25837		1.25809
	v	567.61	2392.82	2.24857	1.25822		1.25805
	VI	562.29	2392.82	2.22737	1.25815		1.25804
					mean		1.25807
					mean .	• ±	0.00001
9.	Ethylen	e under	506•67 mm.*				v
	Ι	510.73	2392.85	2.02220	1.25756		1.25732
	11	505.38	2392.79	2.00086	1.25749		1.25730
	III	515.71	2392.79	2.04194	1.25761		1.25730
	IV	504.45	2392.79	1.99719	1.25750		1.25732
	v	433·18	2392.76	1.71380	1.25662		1.25730
	VI	506·13	2392.79	2.00387	1.25752		1.25733
				mean			1.25731.
						, ±	0.000006
				mean	tor method	(a)	1.257310
				,,	,,	(0)	1.5231315

TABLE I.—THURINGIAN GLASS.—Continued.

Expt. No.	P ₀ .	v.	s.	L_p .	L_0 .
10. Ethyle	ene under i	380 mm.*			
I	383.85	2392.79	1.51799	1.25607	1·2558 2
II	37 ⁸ ·95	2392.79	1.49841	1.25591	1.25572
III	383.83	2392.79	1.51785	1.25602	1.25577
IV	356.76	2392.79	1.41047	1.25271	1.25579
v	382.06	2392.77	1.51072	1.25593	1.25571
VI	372.74	2392.77	1.47389	1.25595	1.25583
VII	379.09	2392.73	1.49901	1.25597	1.25578
VIII	360.07	2392.73	1.42362	1.25582	1.25586
IX	366.55	2392.73	1.44923	1.25579	1.25574
				mean .	. 1·255780 + 0·000017
			mear	n for method (a	1.25577
				Ìb	1.25579
					, 3377

11. Ethylene under 253.33 mm.*

V1	254.48	2392:00	1.00507	1.25451	1.25430
V	228.95	4951.91	1.87098	1.25420	1.25429
IV	252.67	2392.66	0.99794	1.25452	1.25433
III	250.62	2392.66	0.98976	1·25447	1.25425
II	256.74	2392.66	1.01394	1.25449	1.25420
I	230.74	2392.66	0.91112	1.25425	1.25431

111	cun .	•	1 2 3 4 2 0
mean for	method	(a)	1.25431
,,	,,	(b)	1.25427

12. Ethylene under 190 mm.*

Ι	195.48	4951·86	1.59678	1.25368	1.25341
II	191.49	4951.86	1.56424	1.25373	1.25350
III	192.06	4951.86	1.56901	1.25381	1.25358
IV	193.22	4951.86	1.57834	1.25371	1.25346
v	192.60	4951.86	1.57337	1.25376	1.25351
VI	200.91	4951.86	1.64135	1.25384	1.25349
VII	194.42	2392.64	0.76737	1.25371	1.25344
VIII	191.85	4951.86	1.56737	1.25387	1·25363

mean . . 1.253502 ± 0.00002

13. Sulphur dioxide under 760 mm.*

11	764.48	2392.72	7.04640	2.92767	2.92658
III	759.04	2392.72	6 99498	2.92714	2.92654
IV	755.89	2392.72	6.96529	2.92684	2.92652
v	765.70	2392.72	7.05877	2.92775	2.92654
VI	760.23	2392.72	7.00618	2.92724	2.92653
VII	766.13	2392.62	7.06463	2.92783	2.92659
VIII	764·21	2393.74	7.04674	2.92760	2.92653
			mean	• •	. 2.926547 ± 0.00001
			Mean i	for method	(a) 2.92655
			,		(b) 2·92653

* Italicised figures were obtained with gas from method (b); the others by method (a).

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TABLE I.—THURINGIAN GLASS.—Continued.

	Expt. No.	P ₀ .	v.	s.	L _p .	L ₀ .
14.	Sulphu	ır dioxide	under 506.67	mm.		
	I II III IV V VI VII	510.61 507.73 508.47 513.23 506.76 508.54 502.93	2393·50 2393·50 2393·50 2393·50 2393·50 2393·50 2393·50 2393·62	4.671315 4.64429 4.65115 4.69563 4.63538 4.65204 4.60001 mean	2·90487 2·90446 2·90452 2·90513 2·90463 2·90466 2·90468	2.90377 2.90362 2.90357 2.90379 2.90367 2.90374 2.90367 2.90367
				mean : ,,	for method ,,	$\begin{array}{c} \pm 0.000028\\ (a) 2.90369\\ (b) 2.90367\end{array}$

15. Sulphur dioxide under 380 mm.

I	377.20	2393·44	3.43923	2.89291	2.89233
II	379.90	2393.44	3.46129	2.89305	2.89226
III	379.79	2393.44	3.46031	2.89309	2.89230
IV	381-85	2393.44	3.47917	2.89316	2· 89220
v	385.67	2393.44	3.21444	2.89354	2.89223
VI	380.05	2393.44	3.46271	2.89311	2.89231
VII	380.85	2393.56	3.47022	2.89314	2.89227
			mean		2.892271

		•	-	
			±	0.000010
	Mean for	method	(a)	2.89227
- •	**	**	(b)	2.89227

16. Sulphur dioxide under 253.33 mm.*

I	254.49	2393.37	2.30965	2.88190	2.88090
II	249.14	2393.37	2.26074	2.88137	2.88085
шĊ	252.76	2393.49	2.29378	2.88154	2.88069
IV	255.85	2393.49	2.32205	2.88183	2.88070
v	252.33	2393.49	2.28998	2.88164	2.88083
VI	251.49	2393.49	2.28226	2.88156	2.88083
VII	254.48	2393.49	2.30964	2.88184	2.88084
VIII	252.90	2393.49	2.27953	2.88151	2.88080

mean	•	•	•	2.880805
			±	0.000020
mean	for	method	(a)	2.88080
	,,	,,	(b)	2.88082

17. Sulphur dioxide under 190 mm.*

11 III	197.22	2392.64	1.78618	2.87680	2.87518
IV V	190.50	4951.86	3.57239	2.87600	2.87497
vi	174 [.] 37 191·92	2392-04 4951-86	3.59694	2.87637	2.87522
				mean .	. 2.875105 ± 0.000025

TABLE II.---VOLUMETER B (JENA GLASS),

Expt. No.	P_0	υ.	s.	L _p .	L_0 .
1. Oxyge	en (II) unde	r 760 mm.			
I	754.82	2275.19	3.22950	1.428918	1.429000
II	749.30	454 ⁸ ·33	6.40856	1.429110	1 428937
III	763.49	2275 19	3.26656	1.429160	1.428963
IV	763.05	2275.19	3.26456	1.429110	1.428921
v	744.81	4548.33	6.37020	1.429120	1.428952
VI	765.95	2275.19	3.27695	1.429108	1.428910
VII	758.52	2275.19	3.24515	1.429103	1.428916
VIII	765.38	2275.19	3.27459	1.429143	1.428943
IX	748.79	2277.46	3.20673	1.428108	1.428954
				mean .	. 1.428944 ± 0.000010

2. Oxygen (II) under 380 mm.

I	377.78	4548.09	3.22950	1.42850	t·42832
II	382.12	4548.09	3.26656	1.42848	1.42829
III	381.89	4548.09	3.26456	1.42847	1.42828
\mathbf{IV}	383.33	4548.09	3.27695	1.42850	1.42830
v	379.62	4548.09	3.24515	1.42847	1.42828
\mathbf{VI}	383.06	4548.09	3.27459	1.42848	1.42828
VII	375.12	4548.09	3.20673	1.42848	1.42831
				mean .	1.428294

± 0.000005

3. Carbon dioxide (II) under 760 mm.*

I	757·31	2275.19	4.48241	1.97712	1.976896
II	765.17	2275.61	4.53024	1.97732	1.97695
III	768.62	2275.61	4.53073	1.97736	1.976935
IV	761.35	2277.46	4.51112	1.97724	1.97694
v	762.98	2275.61	4.51717	1.97728	1.97695
VI	759.52	2275.61	4.496485	1.97720	1.97693
VII	760.36	2275.61	4.50151	1.97722	1.97694

me	ean			1.976934
			±	0.000002
mean for	met	hod	(a)	1.976934
,,	,,	,	(b)	1.976935

4. Carbon dioxide (II) under 380 mm.*

I	385.33	2275.50	2.27347	1.97055		1.97016
II	381.91	2275.50	2.25313	1.97044		1.97011
III	379.88	2275.50	2.24115	1.97043		1.97015
IV	380.31	2275.50	2.24367	1.97042		1.97013
v	379.88	2275.50	2•24111	1.97040		1.97011
VI	382.01	2275.50	2.25377	1.97048		1.97016
VII	383.94	2275.50	2.26517	1.97049		1.97014
			mean		±	1·970137 0·000011
			mean	for method	(a)	1.970137
			,	, ,,	(b) .	1.970137

						,		
	Expt. No.	P ₀ .	t	·•	s.	L_{p} .		L_{0} .
5.	Sulphur	dioxide	(II) unde	er 760) mm.*			
	Ι	761.08	2275	61	6.67065	2.92721		2.92658
	II	763.19	2275	61	6.68955	2.92739		2.92657
	III	759.92	2275	61	6.66015	2.92706		2.92654
	IV	759.23	2275	61	6.65534	2.92698		2.92652
	v	756.84	2275	61	6.63258	2.92681		2.92656
	VI	762.41	2275.	61	6•68248	2.92729		2.92654
	VII	762.26	2275.	41	6.68058	2.92728		2.92654
					mean			2.02655
					mean	• •	•	2.92055
					mean	for method	$(\alpha)^{\pm}$	2.02655
					mean	ior method	(b)	2.02654
						,, ,,	(0)	2 92034
6.	Sulphur	dioxide	(II) unde	er 380) mm.*			
	Ι	380.31	2275	50	3.29413	2.89294		2.89229
	11	380.80	2275	50	3.29847	2.89302		2.89233
	III	380.83	2275	50	3.29866	2.89296		2.89227
	IV	383.56	2275	50	3.32267	2.89328		2.89234
	\mathbf{v}	381.03	2275	50	3.29672	2.89308		2.89237
	VI	383.68	2275	50	3.32363	2.89321		2.89226
	VII	382.55	2275	29	3.31346	2.89315		2.89230
					mean			2.80221
					mean	• •		2 09231 0.00002
					mean	for method	$(a)^{\pm}$	2.80221
					mean	ior methou	(m) (b)	2.80220
						,, ,,	(0)	<u>~</u> 0y230

TABLE II.-VOLUMETER B (JENA GLASS).-Continued...

The agreement of the mean values by the two methods for ethylene, sulphur dioxide and for carbon dioxide proves furthermore the high purity of the gases employed.

Hydrogen Sulphide.—Some preliminary results obtained with H₂S are recorded,

Pure gas was prepared by hydrolysis of Al_2S_3 , then cooled in a mixture of ice and salt, dried over P_2O_5 , filtered through Schott's filter, bubbled and fractionated. In agreement with the observations of Cardoso and co-workers,' after several fractionations a middle fraction which did not attack mercury was obtained. Moreover, to avoid a possible reaction by long contact, the measurements were undertaken by Regnault's method, using the same apparatus which had previously served for CO_2 , N_2O and $SiF_4.^3$ This was fitted with an Apiezon oil manometer between the barometer and the density bulbs, so allowing pressure equilibrium to be established without contact of the gas and mercury. Hydrogen sulphide dissolves to a very small extent and very slowly in Apiezon oil, so that no trouble arose in this way.

The density bulbs had the capacities : A = 580.955 ml. (after repair, $A_{\pi} = 581.14$). B = 454.735 ml. Corrections are made as usual.

Preliminary attempts to measure adsorption for H_2S show anomalous results, possibly due to reaction with the mercury of the apparatus. On account of its analogy in physical constants with CO₂ and HCl we can provisionally take the value 12×10^{-8} c.c. per cm.² as the coefficient of adsorption.

Results corrected as usual are summarised in Table III in which the symbols have the same significance as above. The compressibility coefficient has been experimentally deduced as before.

* Italicised figures were obtained with gas from method (b); the others by method (a).

⁷ J. Chim. physique, 1912, 10, 504; Gazzetta, 1921, 51, 155.

			IADLE	111.		
Expt. No.	v.	P ₀ .	s.	L _p .	<i>L</i> ₀ .	Mean.
1. Hydrog	en sulphi	de under '	760 mm.*			
I	580.995	755.44	0.888605	1.53867	1.538537	1.538537
II	580.995	777.47	0.91473	1·5390 3	1.538357	\$ 1.538303
	454.735	777.47	0.71596	1.53909	1.538430	{ - 55-595
III	580.995	774 4 I	0.01102	1.23863	1.538327	1.538323
	454.735	774·4I	0.71300	1.23891	1.538320	{
1V	580.995	745.86	0.87708	1.23823	1.238337	1.538423
	454.735	745.80	0.08054	1.53839	1.538510	{
v	580.995	755.00	0.88800	1.53849	1.538307	1.538428
***	454.735	755.00	0.09510	1.53800	1.538490	{
VI	580.995	758.98 .	0.69270	1.53005	1.530427	>1.538418
3777	454.735	758.98	0.09872	1.53002	1.530410	{
VII	580.995	704.59	0.09945	1.53001	1.530457	×1.238498
WIII	454.735	704.59	0.70391	1.53800	1.530340	{
VIII	500.995	767.95	0.90343	1.53007	1.530427	21.238413
īv	454735	707.95	0.70707	1.53803	1.530400	J T+528480
	454 735	702.33	0.80061	1.53860	1 530400	1 330400
А	501.140	750.99	0.60601	1.52866	1.528500	21.238463
XI	434 733 581 · 140	750 99	0.88866	1.53862	1.538487	{
111	151 140	733 33	0.60525	1.53860	1.538480	10538483 ک
	454 / 55	/33 33	0 09333	1 55000)
			п	nean .	1.538426 -	0.000012
			n	nean for (a)	1.538415	
			n	nean for (b)	1.538436	
				• • • •	00 10	

2. Hydrogen sulphide under 380 mm.*

I	454·735	374.07	0.34237	1.52968	<i>1·5294</i> 8 1·52948
II	580.995	383.79	0.44883	1.52976	1.52935 1 1.52028
	454.735	383.79	0·35130	1.52980	1.52941 5 1.52950
III	580.995	383.68	0.44874	1.52990	1.52949 1 1.520275
	454.735	<u>383.68</u>	0.35119	1.52979	1.52936 5 - 5-9375
IV	580.995	337·0 6	0.44094	1.52969	1.52942 1.52028
	454.735	377.06	0.34509	1.52971	1·52934 ∫ ¹ J ² 93 ⁰
v	580.995	375.36	0.43894	1.52965	1.52942 1.52042
	454 [.] 735	375.36	0.34355	1.52967	<i>1</i> ·52944 ∫ ¹ 5 ²⁹⁴⁵
			m	iean .	1.529412 ± 0.000016
			m	ean for (a)	1.529420
			m	ean for (b)	1.529406

As appears from Table IV. the probable errors in the mean values are somewhat fortuitous. There is no strict proportionality between the errors and the measuring pressures. We conclude, then, that the limit of accuracy 10^{-5} is practically reached in practice for every gas at every pressure.

TABLE IV.

p.	O _s	C ₂ H ₄	SO2	O_2	CO2	SO ₂	SH2
1.000	0.20	o ∙85	0.32	o ∙69	o·26	0.32	0·78×10-5
0.750	1.14	o·80				—	_
0.667	1.40	0.20	0.90				_
0.200	0.40	1.35	0.55	0.32	0.22	0.20	1.03
0.333	1.30	1.40	0.20				_
0.220	1.65	1.60	o·85				<u> </u>

Adsorption Correction.

Correction for adsorption on the glass walls of density flasks has been experimentally determined for every gas in our Institute by Crespi.⁸ The

	<i>p</i> = 1.0000.	0.20000	0°25000 atm.
Thuri	ingian glas	s.	
O2	2.0	2.7	3.2×10^{-5} gr.
CŌ,	6.1	9.1	13.2
C₂Ĥ₄	2.8	3.4	4.4
SO ₂	30.0	41.0	57.0
Jena	glass.		
co,	1.2	2.2	\times 10 ⁻⁵ gr.
SO ₂	13.8	23.2	°

TABLE V.

corrections for different pressures expressed in grams per litre are given in Table V.

Comparison has already been made ⁴ between various molecular weights of CO_2 and various atomic weights of carbon, as deduced of the limiting density and employing uncorrected and corrected numbers which lead to differences as great as $C = 12 \cdot 012$ and $12 \cdot 007$. In order to ascertain the accuracy of the

adsorption correction, a direct comparison can be made (Table VI) of the new results for CO₂ and SO₂ with the previous ones deduced by Moles and Toral for CO₂, employing volumeter A with both density bulbs of Thuringian glass and volumeter B of Jena glass and with corrected and uncorrected values.

We see that the corrected values are very reliable, the uncorrected showing differences of 4.5 and 5.5×10^{-5} , which greatly exceeds the limit of accurrent of the

of accuracy of the method. The correction hence becomes fully justified.

The agreement between normal density of CO₂ as measured by Moles and (Miss) Toral in 1936 according to Regnault's method and with density flasks of small capacity (about 500 ml.) and the results of the present paper obtained

TABLE VI.

Gas.			L _p .			
	Method.		Corrected.	Uncorrected		
002	$\begin{cases} Bulb & . \\ Volumeter & B \end{cases}$	•	1·976938 1·976934 0·000004	1.977038 1.976952 0.000086		
50 2	$\begin{cases} Volumeter A \\ Volumeter B \end{cases}$	•	2·926547 2·926550	2·926850 2·926690		

in the volumeter B of Jena glass and capacity from about 2400-4500 ml. is very significant and proves the complete absence of systematic errors.

Density as a Function of Pressure.

As has been established above, Berthelot's rule of the limiting densities applies, within the limits of accuracy required in atomic weight measurements, only if linear extrapolation of the limiting values holds strictly good for all gases over the range of pressure investigated. From preceding results the relationship between L_p and p can be expressed by the equations shown in Table VII.

Whatever be the extreme cases of a less compressible gas, oxygen and an exceedingly compressible one, so far as concerns sulphur dioxide, no differences in behaviour were remarked. Ethylene and sulphur dioxide are of the same type as CO_2 , NH_3 and SiF_4 , with which we have dealt in previous papers. For all, the $L_p - p$ curve is linear within the limits of

⁸ A summary of this work is given in Bull. Soc. chim. Belgique, 1938, 47, 405.

our experimental error, which is of the order of I in 100,000 on an individual ratio. Consequently, $L_p = a + bp$, where a is the limiting density.

TABLE VII.

Þ	L_p obs.	L_p calc.	
Oxygen	(I) $L_p = (1.42761)$	9 ± 0.000005)	+ 0·0001326 . p.
1.00000	1.428948	1.428945	-0.3×10^{-5}
0.75000	1.428600	1.428612	+ 1.2
0.66667	1.428512	1•428503	- 0.9
0.20000	1.428284	1.428282	- 0.3
0.33333	1.428045	1.428061	+ 1.6
0.25000	1.427963	1.427950	- 1.3
Ethylene	e, $L_p = (1.251223)$	± 0.000002) +	0·009134 . <i>þ</i> .
1.00000	1.260359	1.260357	- 0·2 $ imes$ 10 ⁻⁵
0.75000	1.258073	1.258073	± 0.0
0.66667	1.257312	1.257312	± 0.0
0.20000	1.255780	1.255790	+ 1.0
0.33333	1.254280	1.254267	- 1.3
0.25000	1.253502	1.253506	+ 0.4

Sulphur dioxide, $L_p = (2.857957 \pm 0.00005) + 0.068593 \cdot p$.

1.00000	2.926547	2.926550	+ 0.3
o.66667	2.903690	2.903685	0.2
0.20000	2.892271	2.892253	— 1·8
0.33333	2 880805	2.880821	+ 1.6
0.25000	2.875105	2.875105	± 0.0

Discussion of the Results.

As stated above, molecular weights of gases in relation to our oxygen system are deduced according to the rule of the limiting densities of Berthelot from the simple equation

 $M' = 32.000 \cdot r_0,$

where 32.000 is the conventional molecular weight of oxygen and r_0 is the ratio of the limiting densities $L_{\lim}: L^{\circ}_{\lim}$ or the value extrapolated to p = 0 from the partial ratios of the L_p values. We thus obtain from the above the values given in Table VIII.

TABLE VIII.

p.	* p.		r ₀ .	r _p .	r ₀ .
Ratio C ₂ H	$\mathbf{I}_4:\mathbf{O}_2\ (\mathbf{I}).$			Ratio SO ₂ :	O ₂ (I).
1.00000	0.882020			2.04804	
0.75000	0.880631		o·876464		
0.66667	0.880154		0.876422	2.03267	2.00193
0.20000	0.879223		0.876426	2.02500	2.00196
0.33333	0.878320		0.876470	2.01734	2.00198
0.25000	0.877824		0.876425	2.01343	2.00189
	mean		0.876441		2.00194
$r_0 = L_{\lim}$	$L^{\circ}_{lim} =$		0.876441	:	= 2.00193
Ratio CO	2 : O2 (II).			Ratio SO	: O ₂ (II)
1.00000	1.383492			2.04805	
0.20000	1.379362		1.375234	2.02501	2.00197
$r_0 = L_{\lim}$	L°_{\lim} .	•	1.375231		2.00196
Ratio H ₂ S	$S: O_2.$			*	
1.00000	1.07662				
0.20000	1.07080		1.06498		
$r_0 = L_{\lim}$	L°_{iim}		1.06497		

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For the molecular weights it follows

$$\begin{array}{ll} M({\rm C}_2{\rm H}_4) = 28{\cdot}046 & M({\rm CO}_2) = 44{\cdot}0074 \\ M({\rm SO}_2)^1 = 64{\cdot}062 & M({\rm SO}_2)^2 = 64{\cdot}063 \\ M({\rm SH}_2) = 34{\cdot}079 \end{array}$$

and therefore for the atomic weights

as compared with previous values obtained from the limiting densities from CO and CO_2 :

C = 12.0064 and C = 12.007

The general mean of the four different values for carbon leads to

 $C = 12.007 \pm 0.0002$,

which is identical with the reduced physical value on the basis of the most recent results on isotopic weights of carbon,⁹ the relative abundance $C^{12}: C^{13} = 99\cdot3: 0\cdot7$ as accepted in the 3rd Report of the International Committee on Atomic Weights for 1938 and with the most probable conversions factor $1\cdot000275.^{10}$ It is somewhat lower than the accepted value in the International Table $C = 12\cdot010$. The value for sulphur $S = 32\cdot063$ agrees with the accepted international one and agrees also with the physical value referred to chemical scale $S = 32\cdot064$, when the abundance ratio for isotopes, as found recently by A. O. Nier, is taken in account. The error in the third decimal figure should not exceed I or 2 units.

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⁹ Aston, Proc. Roy. Soc., A, 1937, 163, 591; Nature, 1938, 1096. ¹⁰ R. Whytlaw-Gray, Annual Reports, for 1938, 125.