156. *The Compressibilities of Certain Gases at Low Pressures and Various Temperatures.*

By Walter Cawood and Hubert S. Patterson.

In a previous communication (Cawood and Patterson, J., 1932, 2180) we described measurements of the compressibility of methyl fluoride between pressures of 1 and 3 metres, and showed that the relationship between pv and p was certainly linear over the range of pressure investigated; the pv–p straight line could therefore be extrapolated to zero pressure with confidence, and so the compressibility between 0 and 1 atmosphere, which in these circumstances equals the limiting value, could be deduced.

The method has now been applied to other compressible gases at a series of temperatures, including 0°. We have thus been able to find the experimental relationship between the limiting value of the compressibility and the temperature. This relationship is of importance, since various determinations of compressibility in the neighbourhood of 1 atmosphere have been made at temperatures other than 0°, and to enable these data to be applied to calculate the molecular weights of gases from the normal densities, the compressibility at 0° must be found. Hitherto various theoretical equations have been proposed for making this correction, but the compressibilities thus deduced differ from each other and are open to question.

We have also in certain cases obtained data for the limiting value of the compressibility at the critical temperature, in order to test the relationship to which we have previously referred (*loc. cit.*) as holding good between the critical constants and this quantity.

General Considerations.

The gases which we have now investigated are ethylene, carbon dioxide, nitrous oxide, sulphur dioxide, and dimethyl ether. When the experimental values of pv were plotted against the corresponding pressures (from 1 to 3 m. of mercury), in all cases except for dimethyl ether, the relationship was strictly linear within the limit of error of our experiments, and may be represented by :

$$pv = p_0v_0(1 - Ap) \qquad . \; . \; . \; . \; . \; . \; . \; . \; (1)$$

where pv corresponds to the pressure p, and p_0v_0 to zero pressure, A being a constant; since pv and p_0v_0 depend on the amount of gas, it is more convenient to divide each side by p_0v_0, giving an equation of the type

$$pv = 1 - Ap \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (2)$$

These equations are identical in form with those proposed by D. Berthelot (*Compt. rend.*, 1898, **126**, 954) to express the compressibilities of gases at low pressures and so to obtain the limiting densities. We have therefore calculated the slope of our lines by the method of least mean squares, and we obtain from (2) the compressibility coefficient $A = -d(pv)/dp$. Since the lines are straight between pressures of 1 and 3 metres, there is no reason to doubt that they will continue straight down to zero pressure, and that therefore the compressibility coefficient which we measure is also the limiting value.

A similar notation has been used by Rayleigh, but he has used $pv = p_0v_0(1 + \alpha p)$, so that $A = -\alpha$.

The compressibilities measured at high pressures are sometimes expressed by the equation $pv = a + bp + cp^2 + \ldots$, where the terms $p^2 \ldots$ take account of the curvature of the isothermals. For the range of pressure which we have investigated, the curvature is in general quite beyond the limit of error of our measurements, and accordingly, since $a = p_0v_0$ when $p = 0$, this equation becomes $pv = p_0v_0 + bp$, whence $A = -b$.

In order to convert normal densities into their limiting value, they are multiplied by $p_1v_1/p_0v_0 = 1 - A$, p_1v_1 being the value of pv at atmospheric pressure. Now, certain older density determinations have indicated that the pv–p isothermals between pressures of 0 and 1 atmosphere may be markedly curved. We consider these observations to be erroneous, but it is clear that in such a case the above equation of Berthelot would not be valid; p_0v_0 in such circumstances must be obtained by some kind of curved extrapolation, and consequently no physical meaning can be attached to A. For such cases Guye (*J. Chim. physique*, 1908, **6**, 769) suggested a new factor $p_0v_0/p_1v_1 = 1 + \lambda$, which when divided into the normal density gives the limiting density. This notation has been largely adopted and, if the isothermals are straight, it is related to A by the equation $1 + \lambda = 1/(1 - A)$. It must, however, be stressed that this quantity $1 + \lambda$ is merely a ratio, and that λ alone has no simple physical significance like A. Thus it is incorrect to write $pv(1 + \lambda p) = p_0v_0$ and to use an equation of this form to calculate λ from pv measurements made at pressures other than 1 atmosphere, as has sometimes been done. Actually this equation gives pv–p isothermals convex towards the p-axis, which is extremely unlikely both from the form of the high-pressure isothermals and from those calculated from the various equations of state. Equations such as those of van der Waals and of Beattie and Bridgman (*J. Amer. Chem. Soc.*, 1928, **50**, 3151) predict a very slight curvature concave towards the p-axis at low pressures. The amount of curvature calculated lies in most cases within the limit of error of our experiments, but in the case of dimethyl ether, where we have obtained evidence of curvature, the sign is the same as that calculated.

Although A and λ are, in general, small quantities, considerable error may be introduced if they are confused, as appears quite frequently to have been the case in the literature. How large this error may be, will be seen in the tables given, *e.g.*, for dimethyl ether and sulphur dioxide.

EXPERIMENTAL.

C_2H_4 was made from H_3PO_4 and pure EtOH, purified by passage through liquid and over solid KOH, and dried over P_2O_5. It was then solidified, pumped free from air, refractionated a number of times, and finally bubbled through its own liquid.

CO_2 was prepared by heating pure $NaHCO_3$ in vac. It was solidified, pumped free from air, and sublimed three times.

N_2O, obtained from a cylinder, was passed through three bubblers containing conc. H_2SO_4, then through liquid and solid KOH and finally over P_2O_5. The further purification was the same as for C_2H_4; at no stage did the solid or liquid N_2O show any trace of blue colour.

SO_2, made by the action of conc. H_2SO_4 in vac. on Hg, was bubbled through conc. H_2SO_4 and dried over P_2O_5. It was further purified as for C_2H_4.

Me_2O was prepared from pure MeI and NaOMe. It was passed through a vessel surrounded by ice, then through liquid and solid KOH, and dried over freshly prepared CaO. The further purification was similar to that of C_2H_4. We have found that when Me_2O is dried over P_2O_5 some volatile material, possibly a methyl phosphate, is formed; hence a system containing P_2O_5 cannot be completely evacuated even after a long period if it has contained Me_2O. We accordingly avoided any contact with P_2O_5 in our expts. with this ether.

The expts. were carried out in a modified Amagat apparatus with tubes of 4·5 mm. bore. The measurements, unless otherwise noted, were made over pressures of *ca.* 1—3 m. of Hg. The details of the method have been previously described (*loc. cit.*).

Results.

In the following tables are given the values which we have measured for A and $1 + \lambda$ for different gases at various temps. At any one temp. each value of A and $1 + \lambda$ refers to a different filling with the gas.

Ethylene.

	0°.		21°.	
	A.	$1 + \lambda$.	A.	$1 + \lambda$.
	0·0072(2)	1·0072(7)	0·0061(1)	1·0061(5)
	0·0073(1)	1·0073(6)	0·0061(2)	1·0061(5)
Mean	0·0072(7)	1·0073(2)	0·0061(2)	1·0061(5)

Sulphur Dioxide.

	30°.		50°.	
	A.	$1 + \lambda$.	A.	$1 + \lambda$.
	0·0164(2)	1·0167(0)	0·0132(8)	1·0134(6)
	0·0166(4)	1·0169(2)	0·0131(6)	1·0133(3)
Mean	0·0165(3)	1·0168(1)	0·0132(2)	1·0134(0)

Carbon Dioxide.

	0°.		21°.		31°.	
	A.	$1 + \lambda$.	A.	$1 + \lambda$.	A.	$1 + \lambda$.
	0·0067(2)	1·0067(7)	0·0052(1)	1·0052(4)	0·0048(5)	1·0048(8)
	0·0065(3)	1·0065(8)	0·0053(0)	1·0053(3)	0·0048(3)	1·0048(5)
Mean	0·0066(3)	1·0066(8)	0·0052(6)	1·0052(9)	0·0048(4)	1·0048(7)

Nitrous Oxide.

	0°.		21°.		36·5°.	
	0·0069(7)	1·0070(2)	0·0056(4)	1·0056(7)	0·0051(7)	1·0051(9)
	0·0072(4)	1·0072(9)	0·0056(9)	1·0057(2)	0·0049(0)	1·0049(2)
	0·0070(5)	1·0071(0)	—	—	0·0048(9)	1·0049(1)
Mean	0·0070(9)	1·0071(4)	0·0056(7)	1·0057(0)	0·0049(9)	1·0050(1)

Dimethyl Ether.

	0°.		21°.		40°.	
	0·0276(0)	1·0283(8)	0·0207(7)	1·0212(1)	0·0164(4)	1·0167(1)
	0·0270(9)	1·0278(4)	0·0205(5)	1·0209(8)	0·0163(3)	1·0166(1)
	—	—	0·0207(9)	1·0212(3)	—	—
Mean	0·0273(6)	1·0281(1)	0·0207(0)	1·0211(4)	0·0163(9)	1·0166(6)

Methyl Fluoride.

	0°.		21°.		44·5°.	
	0·0115(4)	1·0116(7)	0·0089(3)	1·0090(1)	0·0070(1)	1·0070(6)
	0·0113(1)	1·0114(4)	0·0086(8)	1·0087(5)	0·0070(0)	1·0070(5)
Mean	0·0114(3)	1·0115(6)	0·0088(2)	1·0088(8)	0·0070(1)	1·0070(6)

For the sake of completeness we have included values for MeF taken from our previous work (*loc. cit.*) but altered slightly owing to the adoption of more satisfactory values for the meniscus volumes and capillary depressions. (These alterations make no difference whatever to the conclusions reached in the previous paper.)

In order to indicate the degree of accuracy of our expts., and also to show that within the limit of our exptl. error no curvature is detectable in the pv–p graphs, a few typical results are given. We have selected mainly those at 0°, since any curvature would obviously be greater the lower the temp. The calculated values are those obtained from the least mean square straight lines through the exptl. points.

If the observed results for Me$_2$O are plotted on a large scale, the first three points in each case appear to lie in a straight line, but the last curves away markedly. This is hardly surprising when it is considered that this gas liquefies at 0° under *ca.* 2 m. Accordingly, in calculating the value of A at 0° for this substance, we have only used the first three points, and since the press. range is only about 0·7 m., the results are not comparable in accuracy with those obtained from any of the other isothermals. If in any cases an unsuspected curvature is present, it would tend to make our results for the compressibilities too high.

Gas.	Temp.	Press., mm. Hg.	$pv_{obs.}$.	$pv_{calc.}$.	Diff. $\times 10^5$.	Gas.	Temp.	Press., mm. Hg.	$pv_{obs.}$.	$pv_{calc.}$.	Diff. $\times 10^5$.
CO_2	0°	0·9578	0·99165	0·99176	−11	CO_2	0°	0·9578	0·99164	0·99153	+11
		1·9794	0·98319	0·98298	+21			1·9790	0·98238	0·98250	−12
		2·5804	0·97784	0·97782	+ 2			2·5794	0·97682	0·97719	−37
		2·8717	0·97515	0·97531	−16			2·8696	0·97503	0·97463	+40
N_2O	0	1·0169	0·99063	0·99056	+ 7	SO_2	30	1·0569	0·97728	0·97716	+12
		1·6057	0·98497	0·98510	−13			1·5220	0·96701	0·96711	−10
		2·1089	0·98036	0·98043	− 7			1·9890	0·95692	0·95702	−10
		2·7505	0·97497	0·97448	+49			2·5865	0·94414	0·94411	+ 3
		3·0582	0·97130	0·97163	−33			2·8755	0·93793	0·93786	+ 7
$(CH_3)_2O$	0	0·9386	0·96591	0·96590	+ 1	$(CH_3)_2O$	0	0·9426	0·96639	0·96640	− 1
		1·4886	0·94590	0·94592	− 2			1·4921	0·94700	0·94681	+19
		1·6369	0·94056	0·94053	+ 3			1·6401	0·94137	0·94153	−16
		1·8135	0·93247	—	—			1·8164	0·93297	—	—
C_2H_4	0	1·0119	0·99063	0·99039	+24	$(CH_3)_2O$	21	1·0488	0·97138	0·97164	−26
		1·6014	0·98438	0·98479	−41			1·5154	0·95935	0·95903	+32
		2·1053	0·98011	0·98001	+10			1·9830	0·94645	0·94638	+ 5
		2·7468	0·97392	0·97392	+ 7			2·5809	0·93016	0·93022	− 6
								2·8706	0·92233	0·92236	− 3

Some Theoretical Relationships.

The value of $A = -d(pv)/dp$ which we measure is equal to the limiting value when the pressure is indefinitely small (p. 620). If now we calculate the limiting value of $d(pv)/dp$ from the equations of van der Waals and Dieterici, we find that $d(pv)/dp = b - a/RT$, where b is the term involving the covolume and a that involving the attraction of the molecules. Accordingly, $A = a/RT - b$. If a and b are constant there should therefore be a linear relationship between A and $1/T$. Actually in all cases a slight curvature is obtained due to the variation in the values of a and b with temperature. This curvature is always of the same sign and is in accordance with the observations of van der Waals.

If, however, we empirically plot log A against log T we obtain a much better approximation to a straight line. This is really equivalent to assuming that $A = CT^n$, where C and n are constants. The value of n depends on the gas and the temperature range, varying between about -2 and -4, and being numerically smaller the less condensable the gas and the higher the temperature. The curvature of these log A-log T lines is so small that interpolation or extrapolation over a short range can be undertaken with confidence. Accordingly, we have used our results to obtain the compressibility of ethylene at the critical temperature, 9·5°, and have thus found $A = 0{\cdot}00671$. Similarly, for sulphur dioxide at 0°, we have deduced the value $A = 0{\cdot}0243$ and $1 + \lambda = 1{\cdot}0249$. This value is not so reliable as the value for ethylene, since the extrapolation from 30° to 0° is rather long.

We have also used our curves to correct to 0° the values of the compressibility of certain gases measured by Leduc (*Compt. rend.*, 1898, **125**, 297 ; Berthelot, *J. Physique*, 1899, **8**, 269) and Rayleigh (*Phil. Trans.*, 1905, **204**, 351) at various temperatures. The corrections in these cases should be highly accurate. The results are given in the following table.

Observer.	Gas.	Temp. of obsvtn., t.	Exptl. value of A at $t°$.	Value of A corr. to 0°.	Value of $1 + \lambda$ at 0°.
Leduc	CO_2	16°	0·00526	0·00628	1·00632
,, ...	N_2O	16	0·00590	0·00700	1·00705
,, ...	SO_2	16	0·01915	0·0238	1·0244
Rayleigh	CO_2	15	0·00558	0·00659	1·00663
,, ...	N_2O	11	0·00654	0·00736	1·00741

The extrapolated value for sulphur dioxide is again not so reliable as the others.

At the critical temperature, the compressibility coefficient is theoretically given by $A_c = a/RT_c - b$. By substituting the values of b and a deduced by van der Waals and Dieterici respectively, we obtain the following expressions :

(1) *According to van der Waals.*

Since $$\frac{RT_c}{p_c v_c} = \frac{8}{3}, \qquad A_c = \frac{19}{64}\frac{RT_c}{p_c} = \frac{19}{24}v_c = 0{\cdot}791 v_c.$$

Also, since $$R = \frac{1}{273}, \qquad \frac{A_c p_c}{T_c} = \frac{19}{64}R = \frac{19}{64 \times 273} = 0{\cdot}00109.$$

(2) *According to Dieterici.*

Since
$$\frac{RT_c}{p_c v_c} = \frac{1}{2}e^2, \qquad A_c = \frac{3}{e^2}\cdot\frac{RT_c}{p_c} = \frac{3}{2}v_c = 1{\cdot}5v_c;$$

also
$$\frac{A_c p_c}{T_c} = \frac{3R}{e^2} = \frac{0{\cdot}406}{273} = 0{\cdot}00149.$$

From both of the above equations it will be seen that the limiting value of the compressibility at the critical temperature is directly proportional to the critical volume, *i.e.*, it depends only on the volume occupied by the molecules. It also follows that $A_c p_c/T_c$ should be a constant, although the numerical value differs for the two equations. In each case, however, the constant contains implicitly the ratio $RT_c/p_c v_c$, which theoretically should be the same for all substances but actually varies considerably. The following table tests the constancy of the ratio $A_c p_c/T_c$; * it is evidently not constant, but varies between the values deduced from Dieterici's equation and that of van der Waals, being on the whole much nearer the latter. This might be anticipated since theoretically A_c is proportional to v_c, and a better approximation to v_c is obtained from van der Waals's equation than from Dieterici's.

Gas.	Crit. press., p_c, atmos.	Crit. temp., T_c°, Abs.	A_c.	$10^3 p_c A_c/T_c$.
C_2H_4	50·7	282·5°	0·00671	1·20
CO_2	72·7	304·0	0·00484	1·16
N_2O	71·7	309·5	0·00499	1·16
CH_3F	58·0	317·5	0·00701	1·28

The Compressibilities at 0°.

For the purpose of comparing our data for compressibilities at 0° with those of other observers, we will make use both of measurements made at 0° and also of the values we have deduced from the data of Leduc and Rayleigh.

Ethylene.—Measurements at 0° have been made by Batuecas (*J. Chim. physique*, 1925, **22**, 101), who obtained the value 1·0078, and by Stock and Ritter (*Z. physikal. Chem.*, 1926, **124**, 204), who give 1·0079. Our own experimental value is 1·0073. The measurements of Batuecas were made with a manometer of 14-mm. bore and were not corrected for capillary depressions, which are appreciable. The same criticism applies also to his measurements for carbon dioxide, nitrous oxide, and dimethyl ether. Stock and Ritter's value appears to be vitiated by a miscalculation, since the densities they give, *viz.*, 1·26047 at 750·87 mm. and 1·25658 at 376·22 mm., lead to $1 + \lambda = 1{\cdot}0063$, instead of their 1·0079.

Carbon Dioxide.—In addition to the data of Leduc and Rayleigh, measurements have also been made by Chappuis, Keesom (Academisch Proefschrift, 1904, p. 42), and Guye and Batuecas (*J. Chim. physique*, 1923, **20**, 308). Keesom measured the compressibility at 20°, his mean value being $A = 0{\cdot}005675$. On extrapolation by our experimental curves, the corresponding value at 0° is $A = 0{\cdot}00700$. The following table shows the various values of A and $1 + \lambda$.

Observer.	A.	$1 + \lambda$.	Observer.	A.	$1 + \lambda$.
Leduc	0·00628	1·00632	Rayleigh	0·00659	1·00663
Chappuis	0·00676	1·00681	Guye and Batuecas	—	1·00706
Keesom	0·00700	1·00705	Cawood and Patterson	0·00663	1·00668

The mean value of $1 + \lambda$ is 1·00676. From high-pressure data, Beattie and Bridgman (*loc. cit.*) have deduced $1 + \lambda = 1{\cdot}00682$. The evidence therefore appears to indicate clearly that for this gas $1 + \lambda = 1{\cdot}0067$ or 1·0068, rather than the higher value 1·0071.

Nitrous Oxide.—The data available are given in the following table. Batuecas's

Observer.	A.	$1 + \lambda$.	Observer.	A.	$1 + \lambda$.
Leduc	0·00700	1·00705	Batuecas[1]	—	1·0074
Rayleigh	0·00736	1·00741	Batuecas[2]	—	1·0085
Cawood and Patterson	0·00709	1·00714			

[1] *Loc. cit.*

[2] *J. Chim. physique*, 1931, **28**, 572.

---

* We have chosen to investigate this relationship rather than that between A_c and v_c owing to the uncertainty in the values of the critical volume.

second measurement may be neglected as it appears to be highly improbable when compared with the other data. The mean of the other measurements is $1 + \lambda = 1{\cdot}00725$ compared with our value 1·00714.

Sulphur Dioxide.—Available measurements are :

Observer.	*A*.	$1 + \lambda$.	Observer.	*A*.	$1 + \lambda$.
Leduc	0·0238	1·0244	Jacquerod and Scheuer [2]	0·0238	1·0244
Baume [1]	0·0238	1·0244	Cawood and Patterson	0·0243	1·0249

[1] *J. Chim. physique*, 1908, **6**, 1.

[2] *Compt. rend.*, 1905, **140**, 1384.

Owing to some uncertainty in the extrapolation, our own data and those of Leduc may be slightly in error.

Dimethyl Ether.—Measurements by Baume and by Batuecas (*locc. cit.*) are given :

Observer.	*A*.	$1 + \lambda$.	Observer.	*A*.	$1 + \lambda$.
Baume	0·02656	1·02728	Cawood and Patterson	0·0274	1·0281
Batuecas	—	1·02540			

Batuecas's gas was dried over phosphorus pentoxide and may therefore have been contaminated (see p. 620). His isothermal also is highly curved. Our own data are less reliable for this gas than for the other gases, as the pressure range was only about 70 cm. The most probable value of the compressibility appears to be approximately 0·027.

It is of interest to apply our measured compressibilities to obtain molecular weights from the existing normal densities of the various gases. For this purpose we have taken mean values of the various normal densities of different observers as shown in the following table :

Gas.	Mean normal density.	Observers.
Ethylene	1·2606	Leduc; Stahrfoss; Batuecas; Stock and Ritter.
Carbon dioxide	1·9767	Leduc; Rayleigh; Guye; Guye and Pintza.
Nitrous oxide	1·9777	Leduc; Rayleigh; Guye and Pintza.
Sulphur dioxide	2·9265	Jacquerod and Scheuer; Baume; Cooper and Maas.
Dimethyl ether	2·1100	Baume; Maas and Russell.

For oxygen we have taken only the value of Baxter and Starkeweather, *viz.*, 1·42896, and have assumed $1 + \lambda = 1{\cdot}00094$. From these data the molecular weights have been calculated by means of the formula $M_1 = 32\, D_1(1 + \lambda_2)/D_2(1 + \lambda_1)$, where D_1 and D_2 are the normal densities, D_2 and $1 + \lambda_2$ refer to oxygen, and D_1, $1 + \lambda_1$ and M_1 to the other gas. The data and resulting molecular weights are shown below.

Gas.	Normal density.	$1 + \lambda$.	*M*.	Gas.	Normal density.	$1 + \lambda$.	*M*.
Ethylene	1·2606	1·0073(2)	28·051	Sulphur dioxide	2·9265	1·0249	64·004
Carbon dioxide	1·9767	1·0066(8)	44·014	Dimethyl ether	2·1100	1·0281	46·003
Nitrous oxide	1·9777	1·0071(4)	44·016				

From ethylene we obtain for the atomic weight of carbon C = 12·010, whilst carbon dioxide gives C = 12·014. Both these values are higher than the accepted value C = 12·00, and appear to confirm our previous opinion (*Nature*, 1931, **128**, 375) that the atomic weight of carbon is 12·01 rather than 12·00. Our mean value, 12·012, agrees with that found spectroscopically by Jenkins and Ornstein (*Proc. K. Akad. Wetensch. Amsterdam*, 1932, **33**, 1212), *viz.*, 12·011. Nitrous oxide gives N = 14·008, the accepted value. Sulphur dioxide leads to S = 32·00, and dimethyl ether to C = 11·98, both of which are obviously erroneous, being far too low. In the case of sulphur dioxide, the agreement of the values of different observers for the normal density appears to indicate that the compressibilities measured both by ourselves and by others are too high, which would be the case if adsorption errors were present or the isothermals were slightly curved. As dimethyl ether is also a highly compressible gas, the same errors may also vitiate the results.

We propose to investigate these two highly compressible gases in an apparatus of greater accuracy made of quartz, so that errors due to adsorption will be reduced or eliminated.

We thank Imperial Chemical Industries and the Department of Scientific and Industrial Research for grants. We also express our great indebtedness to Professor Whytlaw-Gray for placing every facility at our disposal and for his continued interest in and criticism of this work.

LEEDS UNIVERSITY.

[*Received, March 27th*, 1933.]