LVI.—*The Molecular Weights of Krypton and Xenon.*

By HERBERT EDMESTON WATSON.

THE densities of krypton and xenon have recently been determined by Moore (Trans., 1908, **93**, 2181), the results being considered accurate to about 1 part in 1000. Now it is known that the compressibilities of these gases are considerable, that of xenon being of the same order of magnitude as that of carbon dioxide, for which the compressibility correction to the molecular weight amounts to nearly 1 per cent. The actual compressibilities between 0 and 1 atmospheres have not been measured, but the critical constants are known with some accuracy, and using these it is possible to apply a correction to the atomic weight.

According to Guye (*J. Chim. Phys.*, 1905, **5**, 5), the molecular weight of the more compressible gases is given by the formula $M = RL/(1 + a_0)(1 - b_0)$, L being the weight of a normal litre, and R the gas constant. Also, $a_0 = a(T_c/T)^{3/2}$ and $b_0 = b(2 - T/T_c)(1 - 0.003229 P_c/P)$, where a and b are the constants in van der Waals' equation calculated by the ordinary means, T_c P_c the critical temperature and pressure, and T P the normal temperature and pressure.

The formula may also be written $M = RL(1 + A)$, where A is the compressibility coefficient between 0 and 1 atmosphere.

Assuming the values for the critical constants given by Ramsay and Travers (*Phil. Trans.*, 1901, **197**, 47), namely, Kr 210.5°, 4124 cm., Xe 287.7°, 4350 cm., a and b may be calculated, and hence A . The values found are -0.00210 and -0.00690 respectively.

It was also found by the same author that for "permanent" gases $M = L(R + 0.0000623 T_c)/(1 + a)(1 - b)$, and if this be again written $M = RL(1 + A)$, the value of A for krypton is -0.00228 . For argon Guye found the figure -0.00120 .

It is interesting to compare these results with those which may be deduced from the actual compressibility measurements of Ramsay and Travers (*loc. cit.*), although as these were only made at pressures greater than 20 metres of mercury, and, moreover, at a temperature of 11.2° , no more than a qualitative significance can be attached to them.

The values given for p_v in the cases of argon, krypton, and xenon were carefully re-plotted, and it was observed that in all three cases they appeared to approximate to a straight line at low pressures. For argon and krypton between 20 and 30 metres of mercury, the curves appeared to be quite straight within the limits of experimental error, whilst with xenon, the curvature was very slight. Assuming the lines to be straight, and extrapolating to zero pressure, the values of $p_0 v_0$ obtained were 1825, 1832, and 1825 respectively, whilst from the quantities of gas taken, the calculated $p_0 v_0$ in each case was 1771. However, the curves for argon and krypton will hardly bear extrapolation to this point, and, in fact, if 1771 were the true value, it would follow that the compressibility coefficient of argon at low pressures is positive, whilst the reverse is known to be the case. Now, it is not difficult to see that the compressibility coefficient is largely affected by a comparatively small change in the absolute value of $p_0 v_0$, so that a small error in measuring the initial volume of gas might alter the former quantity considerably. Details of the amount of gas used for the determinations are not given, but it may be observed that the value of p_v for helium, which remained constant between 20 and 30 metres pressure, and is now known to be constant at one atmosphere, is given as 1742, so that errors of the magnitude of 2 per cent. are not to be excluded. It seems therefore justifiable to take the extrapolated values of $p_0 v_0$ in preference to the theoretical one of 1771.

The values of p_v at 20 metres pressure for argon, krypton, and xenon are respectively 1784, 1714, and 1492, so that if the compressibility be assumed to remain constant between 20 and 0 metres pressure, the values of A are -0.00085 , -0.00244 , and -0.00694 . These measurements were, however, made at 11.2° , and to correct them to 0° it is necessary, according to Lord Rayleigh (*Zeitsch. physikal. Chem.*, 1905, **52**, 705), to multiply the values of A by the factor

$$(\theta_0^{-1} - 6\theta_0^{-3})/(\theta^{-1} - 6\theta^{-3}),$$

where $\theta_0 = 273/T_c$ and $\theta = (273 + 11.2)/T_c$. If this be done, the values -0.00103 , -0.00288 , and -0.00798 are obtained.

The following table shows the values of $-A \times 10^5$ calculated by the three different methods:

	Ar.	Kr.	Xe.
Compressibility	103	288	798
Guye (1)	84	210	690
„ (2)	81	228	508

Of these, the last figure for xenon may be discarded, as the method used is only applicable to the less compressible gases, and, for the same reason, the last figure for krypton is probably less accurate, although the difference is not great. With argon the compressibility between 1 and 2 atmospheres pressure has been directly determined, although not very accurately, by Lord Rayleigh (*Phil. Trans.*, 1902, A, **198**, 417). The value of A is given as -0.00042 , that of oxygen being -0.00048 . A later determination for oxygen (*Zeitsch. physikal. Chem.*, *loc. cit.*) gave -0.00094 , a figure which corresponds very nearly with the one recently found by Burt and Gray (*Trans.*, 1909, **95**, 1666), namely, -0.000964 . If the ratio between the compressibilities given in the first paper is correct, the compressibility of argon will thus be about -0.00082 , which is almost identical with the calculated value. It may, however, be observed that the mean value calculated for oxygen by these two methods is -0.00085 . This is due to the fact that the gas constant was taken as 22.412 , whilst 22.415 is found from experiments with oxygen itself. Consequently the true value for the compressibility of argon is probably -0.00093 , although, in order to calculate the atomic weight with 22.412 as gas constant, the lower value must be used.

Bearing these considerations in mind, it seems that the most probable values for the compressibilities of the three gases are not far from -0.00093 , -0.00215 , and -0.00690 respectively.

The comparative nearness of these figures to those deduced from the compressibility measurements lends considerable confirmation to the accuracy of the methods employed, especially if it be borne in mind that the coefficients at 1 atmosphere pressure are almost certain to be somewhat smaller numerically than at 25.

With regard to the atomic weights of krypton and xenon, the following table gives the mean values, L , for the weight of a normal litre calculated from Moore's figures, and corrected to latitude 45° . The second column shows the pressure at which the gas was measured, and the third the value of RL , R being taken equal to 22.412 . The last column gives the values of $RL(1 + A.p/760)$, that is to say, of the molecular weight of the gas:

	L (grams).	p (mm.).	RL .	Mol. wt.
Kr	3.706	475	83.06	82.95
	3.706	772	83.06	82.88
Xe	5.838	446	130.84	130.31
	5.834	521	130.74	130.12

Finally, for the sake of comparison, a table may be given showing the weights of a normal litre measured under 760 mm. pressure, the compressibility coefficients, and the molecular weights of all the inactive gases, although unfortunately there seems to be no obvious connexion between any of these figures:

	L (grams).	$A \times 10^5$.	Mol. wt.
Helium	0·1782	0	8·994
Neon	0·9002	105	20·200
Argon	1·7809	- 93	39·881
Krypton	3·708	- 215	82·92
Xenon.....	5·851	- 690	130·22

UNIVERSITY COLLEGE,
LONDON.