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THE ATOMIC WEIGHT OF HYDROGEN.

BY GRINNELL JONES.

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In 1908, W. A. Noyes[1] published a table giving the results of all the chemical determinations of the atomic weight of hydrogen, and showed by a careful criticism and comparison that the only data obtained by the chemical methods which need to be considered in selecting the most probable value are those published by Morley[2] in 1895, and by Noyes[3] in 1907.

Noyes states that "densities of gases corrected to the condition of an ideal gas by the method of D. Berthelot may be considered as direct comparisons with oxygen, and molecular and atomic weights calculated from these densities should be included with those determined by chemical methods." But he does not add the results obtained by these physico-chemical methods to his table or discuss their value in selecting the most probable atomic weight of hydrogen.

The object of the present paper is to collect the results which have been obtained by the physico-chemical methods and compare them with the result obtained by the chemical methods. In a few cases the results have been recalculated with the use of the most reliable densities of hydrogen and oxygen at present available, namely, those of Morley. In a few cases other minor corrections have been made and the calculations carried out to one more decimal.

D. Berthelot's[4] "method of limiting densities" for calculating exact molecular weights is based on the deduction from the kinetic theory of gases that all gases approach the ideal gas as the pressure is reduced, and that at infinitesimal pressure, Avogadro's hypothesis is strictly true. This may be expressed in more mathematical language as follows: The limit of the ratio of the densities of two gases as the pressure approaches zero is equal to the ratio of the molecular weights of the gases. Berthelot shows in a very simple manner that these relationships may be expressed by

$$M/M' = (1 - A_0^1)D/(1 - A'^1_0)D',$$

where M and M' are the molecular weights of the two gases, D and D' are the densities under normal conditions, and A_0^1 and A'^1_0 are the mean coefficients of the deviation from Boyle's law per atmosphere at

[1] THIS JOURNAL, 30, 7 (1908). See also discussion of this subject by Brauner in Abegg's "Handbuch der anorganische Chemie," Vol. II, Part 1, page 9.

[2] Morley, "Smithsonian Contributions to Knowledge," 1895.

[3] THIS JOURNAL, 29, 1718 (1907).

[4] *J. physique* (3), 8, 263 (1899).

0°, between zero pressure and one atmosphere. This coefficient is defined by the relation

$$d(PV)/PVdP = -A,$$

which gives the value of A at any pressure, P, and corresponding volume, V. The negative sign has been inserted simply for convenience, since without this convention A would be negative for all gases except hydrogen and helium, under normal conditions. It has been shown experimentally by Rayleigh[1] and Chappuis,[2] and theoretically by Berthelot,[3] that for the gases formerly called "permanent" the value of A does not vary with the pressure by an appreciable amount below two atmospheres pressure. Therefore, the value A_0^1 can be taken equal to the value of this coefficient as determined experimentally by Leduc and Sacerdote,[4] Rayleigh,[5] Chappuis,[6] Berthelot,[7] and Jacquerod and Scheuer[8] at pressures up to two atmospheres. Although this procedure necessarily involves an extrapolation, the kinetic theory of gases indicates that this extrapolation is a comparatively safe one.

The following table gives the values for A_0^1 and $1-A_0^1$ for hydrogen and oxygen found by different experimenters:

	Hydrogen.		Oxygen.	
	A_0^1.	$1-A_0^1$.	A_0^1.	$1-A_0^1$.
Leduc and Sacerdote..........	—0.00064	1.00064	0.00076	0.99924
Rayleigh....................	—0.00053	1.00053	0.00094	0.99906
Chappuis....................	—0.00058	1.00058	.....	.....
Jacquerod and Scheuer........	—0.00052	1.00052	0.00097	0.99903
Berthelot....................	—0.00060	1.00060	0.00085	0.99915

The last three experimenters worked at 0°. Rayleigh worked at about 11°, finding at this temperature —0.00052 for hydrogen and +0.00076 for oxygen. He corrected his results to 0° by means of a formula proposed by Berthelot[9] after a careful study of Chappuis' excellent experimental results on this subject. Leduc and Sacerdote found A for oxygen at 16° to be +0.00061, and then corrected this result to 0° by means of a complex empirical formula burdened with numerous em-

[1] *Phil. Trans.*, **198**A, 417 (1902); **204**A, 351 (1905).

[2] Chappuis, "Nouvelles Études sur les Thermomètres a Gaz." Travaux et Mémoires du Bureau International des Poids et Mesures, Vol. XIII.

[3] Berthelot, *loc. cit.* Also "Sur les Thermomètres a Gaz." Travaux et Mémoires du Bureau International des Poids et Mesures, Vol. XIII.

[4] Leduc and Sacerdote, *Compt. rend.*, **125**, 297 (1897). Leduc, *J. physique* (3), **7**, 5 (1898).

[5] Rayleigh, *loc. cit.*

[6] Chappuis, *loc. cit.*

[7] Berthelot, *Compt. rend.*, **145**, 182 (1907).

[8] Jacquerod and Scheuer, *Compt. rend.*, **140**, 1384 (1905); *Mem. Soc. Phys. Hist. Nat. Geneve,* **35**, 659 (1908).

[9] Berthelot, *Sur les Thermomètres a Gaz. l. c.*

pirical constants, obtaining +0.00076. I have made this correction by means of Berthelot's formula and obtained +0.00083. The necessity for applying this temperature correction of course diminishes the reliability of these results. Fortunately, we have compressibility measurements made at 0°. In the case of hydrogen, the value of A varies so little with the temperature that the method of applying the correction is unimportant.

Leduc and Sacerdote did not use their data to calculate atomic weights by the method of limiting densities. When Berthelot first proposed this method, he calculated from these measurements of the compressibility and Leduc's measurements of the densities of hydrogen and oxygen that the atomic weight of hydrogen is 1.0072. There can, however, be little doubt that the density measurements of Morley are the most accurate at present available.[1] Berthelot[2] has recently repeated this calculation, using Morley's densities, and obtained 1.0077 (1.00768). If we correct Leduc and Sacerdote's measurement of the compressibility of oxygen to 0° by Berthelot's method, this result becomes 1.00775, which is probably the best result which can be derived from these measurements.

Similarly, Rayleigh used his own values for the densities and obtained 1.0086, which he admitted to be too high. He did not combine his excellent compressibility measurements with Morley's densities, but when this is done we obtain 1.00775.

Jacquerod and Scheuer used Morley's value for the density, so their result stands, 1.00777.

Berthelot has not yet used his compressibility measurements to calculate atomic weights so far as I have been able to find. His measurements lead to 1.00773.

Unfortunately, Chappuis did not make any experiments with oxygen. His work on hydrogen is very thorough, and is a very valuable confirmation of the calculations made above.

Guye's[3] method for the reduction of the critical constants is based on van der Waals' equation, the constants a and b being calculated from the critical constants. Unfortunately, van der Waals' equation is only an approximation, and for this reason Guye finds it necessary to insert in his formula another term involving the critical pressure and an arbitrary empirical constant. For gases whose critical temperature is above 0°, he finds it necessary to adopt a different and more complex method, involving two empirical constants. Although the method gives results in good agreement with those obtained by chemical methods in most

[1] See Guye, This Journal, **30**, 143 (1908).

[2] Berthelot, *Compt. rend.*, **144**, 78 (1907).

[3] *J. chim. phys.*, **3**, 321 (1905), and many other articles.

cases, it hardly deserves as serious consideration as the chemical method or Berthelot's method of limiting densities in selecting the most probable value of an atomic weight. Guye,[1] using Morley's values for the densities, and Dewar's values for the critical constants of hydrogen (Tc = 32, Pc = 19.4), and Olszewski's values for the critical constants of oxygen, has calculated the atomic weight of hydrogen to be 1.00765. If we substitute Olszewski's[2] recent data for the critical constants of hydrogen (Tc = 32°, Pc = 13.4 to 15), we obtain 1.0078.

Berthelot[3] has criticized Guye's method on theoretical and mathematical grounds and proposed a method of his own for the calculation of the correction to the ratio of the densities by the help of the critical constants. This method is based upon a modified form of van der Waals' equation, which Berthelot[4] proposed after a careful consideration of Chappuis' wonderful experimental work on hydrogen, nitrogen, and carbon dioxide under conditions not very far removed from normal. Berthelot calls this method the method of "indirect limiting density," but it would seem to be more appropriate to call it Berthelot's method of "critical constants," since the critical constants are used instead of the compressibility as in Berthelot's "direct limiting density" method. Berthelot, using the critical constants of Wroblewski, which have recently been confirmed by Olszewski, has calculated the atomic weight of hydrogen to be 1.0076. The critical pressure of hydrogen is not known with sufficient accuracy to determine the fourth decimal place by this method, even if we assume that the formula is exact.

Leduc,[5] using his method of molecular volumes, calculates the correction which must be applied to the ratio of the densities of gases by means of a very complex formula containing six empirical constants. Although a result obtained in this way has very little value as proof of an exact atomic weight, Leduc's result is included for the sake of completeness and to show that its evidence does not conflict. Leduc, using his own values for the densities, obtains H = 1.0073. If, however, we combine Morley's values for densities with Leduc's correcting factor, we obtain H = 1.00765.

In the following table the final corrected results are collected. The name before each number does not necessarily mean that the number can be found in the literature in an article published by the given author. In the case of the method of limiting densities, the numbers have been calculated by Berthelot's method from the experimental data on compressibility, found by each authority named. In the case of the other

[1] *Compt. rend.*, **138**, 1213 (1904).
[2] *Ann. chim. phys.* (8), **8**, 193 (1906).
[3] *Compt. rend.*, **144**, 78, 194 (1907).
[4] *Sur les Thermometres a Gaz. loc. cit.*; also *Compt. rend.*, **144**, 76, 194 (1907).
[5] *Compt. rend.*, **148**, 407, 548 (1909).

physico-chemical methods, the name indicates the method of calculation used. All the results are derived from Morley's values for the densities (except, of course, the results of the chemical methods which are independent of these results):

THE ATOMIC WEIGHT OF HYDROGEN.

Chemical methods:	
Morley	1.00762
Noyes	1.00787
Mean of chemical methods	1.00775
Method of limiting density:	
Leduc and Sacerdote	1.00775
Rayleigh	1.00775
Jacquerod and Scheuer	1.00777
Berthelot	1.00773
Mean	1.00775
Method of critical constants:	
Guye (Dewar)	1.00765
Guye (Olszewski)	1.0078
Berthelot (Wroblewski, Olszewski)	1.0076
Method of molecular volumes:	
Leduc	1.00765

All of the physico-chemical results fall within the limits of the best chemical data. The wonderful agreement of the results obtained by the method of limiting density shows that the compressibility data are probably very accurate, and that the largest source of error in these results is probably Morley's density of hydrogen.

The conclusion drawn by Noyes from the chemical methods that 1.00775 is the most probable value for the atomic weight of hydrogen, is confirmed in a very striking manner by the method of limiting densities, which, as has been pointed out, is the most reliable of the physico-chemical methods.

URBANA, ILL., February 2, 1910.

THULIUM.

(PRELIMINARY ANNOUNCEMENT.)

BY C. JAMES.

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The writer has obtained about 250 grams of the bromate of Cleve's thulium by the continued fractionation of the rare earth bromates more soluble than erbium.

This earth, discovered in 1879, has hitherto never been obtained in a pure condition. It is very rare, and comparatively large amounts of the ytterbiums are obtained during its preparation.