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## THE SIGNIFICANCE OF THE DENSITY OF HYDROGEN BROMIDE WITH REFERENCE TO THE ATOMIC WEIGHT OF BROMINE

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The numerous researches upon the densities of various gases, carried out under the direction of P. A. Guye at the University of Geneva have furnished very interesting information as to the molecular weights of the substances examined, and either directly or indirectly as to the atomic weights of the various elements involved. These experiments have been executed with exceptional care and skill, and represent a great advance in the technique of both the preparation of pure gases and the experimental determination of gas densities.

The values found for the atomic weights in most cases corroborate in such a reassuring way the results of older methods involving gravimetric ratios between solid, and sometimes liquid, substances, that the Swiss investigators have been led to assign a significance to the gas density results which possibly is in excess of their real value. Recently, for instance, Guye<sup>1</sup> has applied the results of experiments upon the density of hydrogen bromide to the determination of the atomic weight of bromine and, partly on this basis, partly on other grounds, insists upon a correction for the atomic weight of silver. Questions concerning the atomic weight of silver have already been dwelt upon in some detail in two preceding papers.<sup>2</sup> The purpose of the present paper is to call attention to some uncertainties involved in the gas density method of determining molecular weights, as applied in the case under consideration.

In the discussion referred to above, Guye computes the molecular weight of hydrogen bromide by a modification of Berthelot's "limiting density" method. In the expression used

$$M = 32 \frac{d_{\text{HBr}}}{d_{\text{O}_2}} \times \frac{(1 + \lambda)_{\text{O}_2}}{(1 + \lambda)_{\text{HBr}}}$$

$d$  represents the weight of the normal liter and  $1 + \lambda$  is equal to  $\frac{P_0 V_0}{P_1 V_1}$ ,

the ratio of the values of  $PV$  at zero pressure and 1 atmosphere respectively. The value of  $M$  thus depends directly upon four experimentally determined quantities, namely, the two densities and the two values of  $1 + \lambda$ . The last two values obviously cannot be measured directly, but must be found by extrapolation from values determined at pressures between zero and one atmosphere. It is clear that where the value of

<sup>1</sup> Guye, *J. chim. phys.*, **17**, 171 (1919).

<sup>2</sup> Baxter, *THIS JOURNAL*, **44**, 577, 591 (1922).

$1 + \lambda$  is not far from unity, as in the case of oxygen, the extrapolation can be done with far greater certainty than with a gas like hydrogen bromide where  $1 + \lambda$  is very nearly 1.01.

Of the two densities, that of oxygen is unquestionably known with the greater accuracy, for the uncertainty is no greater than a few parts in one hundred thousand. Lord Rayleigh's value for the weight of the normal liter, 1.42904 g., has been used by Guye in the foregoing formula. The value of  $1 + \lambda$  for oxygen used by Guye, 1.00097, probably represents an accuracy nearly if not quite as great as that of the density of oxygen.

The chief uncertainties fall, therefore, upon the data referring to hydrogen bromide. As regards the density of the gas, three determinations of the density of hydrogen bromide have been carried out at the University of Geneva, by Moles,<sup>3</sup> by Reiman<sup>4</sup> and by Murray.<sup>5</sup> The gas was prepared by many different methods and the experiments were carried out in globes of different capacities. The divergences do not group themselves in any systematic manner, so that the results may be treated either as one single series or separately in the case of different experimenters, the method which has actually been followed by Guye. In the final discussion Guye rejects the experiments by Murray as being on the whole less reliable than the others.

In all, 33 determinations of the density were made by Moles at atmospheric pressure, varying from 3.64608, to 3.64298, an extreme difference of 0.00310, or 0.085%. The probable error of the mean is  $\pm 0.00008$ , or 0.002%. Reiman made 31 determinations varying from 3.64694 to 3.64199, with an extreme difference of 0.00495 or 0.134%. The probable error is  $\pm 0.00014$ , or 0.004%.

The averages of the two series, 3.64442 and 3.64419, are subsequently subjected to various small corrections<sup>6</sup> and become 3.64441 and 3.64404. It seems probable that the mean value, 3.64423, represents this constant with an accuracy of 0.01%, but in view of the rather disconcerting variation of the individual determinations and the commonly recognized principle that the probable error as calculated by the method of least squares is likely to lead to a false idea of accuracy in a series of less concordant experiments, it is questionable whether the real accuracy is greater than the above estimate.

The values of  $1 + \lambda$  for hydrogen bromide are found from the experimental values for  $PV$  at 1,  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres. To do this the weight of a liter of gas at  $0^\circ$ , and at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres is first found by ex-

<sup>3</sup> Moles, *J. chim. phys.*, **14**, 389 (1916).

<sup>4</sup> Reiman, *ibid.*, **15**, 293 (1917).

<sup>5</sup> Murray, *ibid.*, **15**, 334 (1917).

<sup>6</sup> Ref. 1, pp. 174, 181.

periment. The ratios of  $\frac{2}{3}$  and  $\frac{1}{3}$  the weight of a liter at 1 atmosphere to the weights of one liter at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres give the values of  $PV$  referred to the product at 1 atmosphere taken as unity.

Moles's corrected value for the density at  $0^\circ$  and  $\frac{2}{3}$  atmosphere is  $2.42203 \pm 0.00019$  with an extreme difference of 0.00297 or 0.12%, while Reiman's result is  $2.42190 \pm 0.00023$  with an extreme difference of 0.00606 or 0.25%.

At  $\frac{1}{3}$  atmosphere Moles's figure is  $1.20737 \pm 0.00015$  with an extreme difference of 0.00254 or 0.21% and Reiman's is  $1.20721 \pm 0.00009$  with an extreme difference of 0.00241 or 0.20%.

Since even the "probable errors" of the means at  $\frac{2}{3}$  atmosphere are 0.008% and 0.010%, while those at  $\frac{1}{3}$  atmosphere are 0.012% and 0.008%, it seems very doubtful whether the values of the densities at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres, and therefore the values of  $PV$  which are directly proportional to them, are known with an accuracy of  $\frac{1}{10000}$ .

Furthermore, it is noticeable that the values obtained by Reiman are consistently lower than those obtained by Moles by about 0.01%. The two series of results are summarized in the following table.

$P$ Atmospheres	Moles	Reiman	Difference	Percentage difference
1	$3.64441 \pm 0.00008$	$3.64404 \pm 0.00014$	-0.00038	-0.010
$\frac{2}{3}$	$2.42203 \pm 0.00019$	$2.42190 \pm 0.00023$	-0.00013	-0.005
$\frac{1}{3}$	$1.20737 \pm 0.00015$	$1.20721 \pm 0.00009$	-0.00016	-0.013

From these figures the values of  $PV$  at different pressures referred to that at one atmosphere as unity can be computed by the method outlined on pp. 596-7. The figures in parentheses are calculated from the densities found by Moles. The others are those used by Guye.<sup>7,8</sup>

$P$ Atmospheres	Moles $PV$	Reiman $PV$
1	1.000000	1.000000
$\frac{2}{3}$	(1.003127)	1.003077
$\frac{1}{3}$	(1.006157)	1.006190

Extrapolation of these figures for zero pressure was done by various methods, of which the two upon which most reliance is placed will be discussed. One of these is the "method of secondary differences,"<sup>9</sup> which is

<sup>7</sup> Ref. 1, p. 181.

<sup>8</sup> This discrepancy appears in Moles's paper, (Ref. 3, p. 431) and also in Guye's (*J. chim. phys.*, **17**, 181 (1919)). In both places the weight of one liter of gas at 760 mm. seems to have been incorrectly calculated from the weights at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmosphere.

<sup>9</sup> A simpler method of applying this method is as follows:  $(PV)_0 = (PV)_{\frac{1}{8}} + ((PV)_{\frac{1}{8}} - (PV)_{\frac{2}{8}}) + ((PV)_{\frac{1}{8}} - (PV)_{\frac{2}{8}}) - ((PV)_{\frac{2}{8}} - (PV)_{\frac{1}{8}}) = (PV)_{\frac{1}{8}} - 3(PV)_{\frac{2}{8}} + 3(PV)_{\frac{3}{8}}$ .

illustrated by the following examples. The figures in parentheses represent extrapolated values.

<i>P</i> Atmospheres	Moles (Uncorr.)		
	<i>PV</i>	$\Delta_1 \times 10^6$	$\Delta_2 \times 10^6$
1	1.000000		
$\frac{2}{3}$	1.003105	3105	8
$\frac{1}{3}$	1.006218	3113	(8)
0	(1.009339)	(3121)	
<i>P</i> Atmospheres	Moles (Corr.)		
	<i>PV</i>	$\Delta_1 \times 10^6$	$\Delta_2 \times 10^6$
1	1.000000	3127	
$\frac{2}{3}$	1.003127	3030	97
$\frac{1}{3}$	1.006157	(2933)	(97)
0	(1.009090)		
<i>P</i> Atmospheres	Reiman		
	<i>PV</i>	$\Delta_1 \times 10^6$	$\Delta_2 \times 10^6$
1	1.000000	3077	
$\frac{2}{3}$	1.003077	3113	36
$\frac{1}{3}$	1.006190	(3149)	(36)
0	(1.009339)		

It is noticeable that while Moles's uncorrected results give a value for  $(PV)_0$  which is identical with that of Reiman in spite of the divergence of the individual density values, when Moles's results are corrected for apparent errors in calculation the divergence is pronounced, amounting to 0.025%. This affects the atomic weight of bromine by 0.02 unit.

Since the values of  $PV$  are inversely proportional to the density at any pressure, an error of 0.01% in any one value of the density has a marked influence upon the extrapolated value of  $(PV)_0$ . For instance in the following two tables the values of  $PV$  at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmospheres are respectively increased by 0.01% over the experimental values found by Reiman.

<i>P</i> Atmospheres	<i>PV</i>	$\Delta_1 \times 10^6$	$\Delta_2 \times 10^6$
1	1.000000		
$\frac{2}{3}$	1.003177	3177	164
$\frac{1}{3}$	1.006190	3013	(164)
0	(1.009039)	(2849)	

1	1.000000		
		3077	
$\frac{2}{3}$	1.003077		136
		3213	
$\frac{1}{3}$	1.006290		(136)
		(3349)	
0	(1.009639)		

In both cases the percentage effect upon the extrapolated value of  $(PV)_0$  is *three times as large* as the assumed difference, but in *opposite directions*. Thus an experimental error of 0.01% in the density at either  $\frac{2}{3}$  or  $\frac{1}{3}$  atmosphere affects the molecular weight of hydrogen bromide and the atomic weight of bromine by 0.03% or 0.024 unit. Such an error is admittedly within the experimental error of the density determinations. Because of this greater sensitiveness to experimental error at the lower pressures, it is unfortunate that less attention seems to have been given to the determinations under these conditions.

A second method of extrapolation upon which reliance is placed is the "algebraic method," with the use of equations of the following type

$$PV = 1 + \alpha - aP - bP^2$$

although in reality there is no difference between this method and the former one.

Obviously the last two terms disappear when  $P = 0$ . Then  $(PV)_0 = 1 + \alpha = 1 + \lambda$ . The term  $\alpha$  is found by solution of three equations involving three values of  $PV$ .  $PV$  and  $P$  at one atmosphere are both assumed to be unity.

$$\alpha = \left( (PV)_2 - 1 \right) \frac{P_3}{(1 - P_2)(P_3 - P_2)} - \left( (PV)_3 - 1 \right) \frac{P_2}{(1 - P_3)(P_3 - P_2)}$$

If  $P_2$  and  $P_3$  are taken as  $\frac{2}{3}$  and  $\frac{1}{3}$ , respectively, the expression simplifies to the form

$$\alpha = -3(PV)^{2/3} + 3(PV)^{1/3}$$

and

$$(PV)_0 = 1 - 3(PV)^{2/3} + 3(PV)^{1/3}.$$

Mathematically this method is identical with the "method of secondary differences" (see p. 597) and of course gives results identical with those of the latter method and equally sensitive to errors in the experimental values of  $PV$  from which the value of  $\alpha$  is computed; that is, a given percentage error in the experimental value of  $PV$  at  $\frac{2}{3}$  or  $\frac{1}{3}$  atmosphere is multiplied three times in the value of  $1 + \alpha$ , and hence in the molecular weight of hydrogen bromide.

Upon the assumption that each experimental value upon which the final value of the molecular weight of hydrogen bromide is dependent is in error by 0.01%, and upon the assumption that the effects of all errors are in the same direction, the sum total is 0.07%.

Pressure atmosphere	Density error %	Effect of error %
1	+0.01	+0.01
$\frac{2}{3}$	-0.01	+0.03
$\frac{1}{3}$	+0.01	+0.03
	Total	<hr/> +0.07

In view of this unlikely but not impossible unfortunate combination of circumstances, the molecular weight of hydrogen bromide as found by this method is uncertain by 0.07% or 0.056 unit, and a similar uncertainty exists in the atomic weight of bromine.

While it is only fair to say that the above estimate of the error of the method is probably excessive, even if the total effect were only  $\frac{1}{3}$  as large, the uncertainty in the atomic weight of bromine would be 0.019 unit. It is unlikely that the present uncertainty in the value of the atomic weight of bromine referred to oxygen is as much as 0.01 unit, while the ratio of bromine to silver is apparently known with far greater accuracy.

From Moles's results Guye calculates the atomic weight of bromine to be 79.923, from Reiman's 79.915, from the average density, 79.920. The foregoing considerations indicate that the concordance of this result with that of the gravimetric ratio of bromine to silver<sup>10</sup> (79.916 if Ag = 107.88; 79.909, if Ag = 107.87) is in considerable measure fortuitous.

### Summary

The foregoing brief discussion illustrates some of the pitfalls which beset the gas density method of determining molecular weights. No method of extrapolation can be satisfactory or convincing where, as in this case, the accuracy of the numerical data diminishes as the region to be extrapolated is approached. The conclusion cannot be avoided that while in the case of hydrogen bromide the gas density method of determining molecular weights may be looked upon as an interesting and satisfactory corroboration of gravimetric evidence, its value ceases at that point. To use such evidence as a criterion upon which to judge the best gravimetric evidence, cannot be justified upon scientific grounds.

On the other hand, from the standpoint of the universal application of Avogadro's hypothesis to gases at low pressures, the results of the very careful density determinations in the laboratory of Professor Guye are particularly significant and convincing.

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<sup>10</sup> Baxter, *Proc. Am. Acad.*, **42**, 201 (1906); *THIS JOURNAL*, **28**, 1322 (1906); *Z. anorg. Chem.*, **50**, 389 (1906).