

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 292]

The Density of Ammonia at Reduced Pressures and its Relation to the Atomic Weight of Nitrogen, the Gas Constant, R , and the Limiting Molal Volume, V_0

BY GERHARD DIETRICHSON, C. W. ORLEMAN AND CHARLES RUBIN

Introduction

Density determinations at reduced pressures are of particular importance because of the various computations that are thus made possible. The only previous work recorded, in the case of ammonia, is that by Moles and Batuecas.¹ Using the same method employed in determining the normal density,² they obtained the values

$\frac{2}{3}$ atm.....	0.511815 g./l.
$\frac{1}{2}$ atm.....	.382925 g./l.
$\frac{1}{3}$ atm.....	.254607 g./l.

On the basis of these densities, combined with the previously determined normal density of 0.77169, they found the molecular weight of ammonia to be 17.032 and the atomic weight of nitrogen to be 14.009.

Procedure

The present work was carried out along precisely the same lines as that by Dietrichson, Bircher and O'Brien³ in determining the normal density of ammonia. A number of preliminary experiments had been made by them at each of the pressures, two-thirds and one-third of one atmosphere, using the five-liter Pyrex bulb for measuring the volume of the gas. The latest results have all been obtained with the one-liter Jena glass bulb. In connection with these determinations it is desired to emphasize once more the precautions observed in eliminating the adsorbed ammonia in the line. This was accomplished in two ways. In some cases it was removed by evacuating over a period of fifteen hours, the pumping being interrupted from time to time and dry air admitted. Figure 1 shows the arrangement that was used in other instances. In these cases the adsorbed ammonia was first condensed in bulb A. Stopcock No. 1 was then closed during the subsequent condensation from the one-liter bulb. The condensing bulbs were similar to those used in the previous work. Also, the ammonia was subjected to the same purification process. Allowance was made in all of these experiments for the change in volume of the five-liter and the one-liter bulbs with pressure.

(1) Moles and Batuecas, *Anales Soc. Españ. fis. quim.*, **28**, 871 (1930).

(2) Moles and Batuecas, *Sitz. Akad. Wiss. Wien*, **138**, 779 (1929).

(3) Dietrichson, Bircher and O'Brien, *THIS JOURNAL*, **55**, 1 (1933).

Experimental Data

Nine determinations were made at two-thirds of an atmosphere using the five-liter bulb and six with the one-liter bulb. Table I contains these

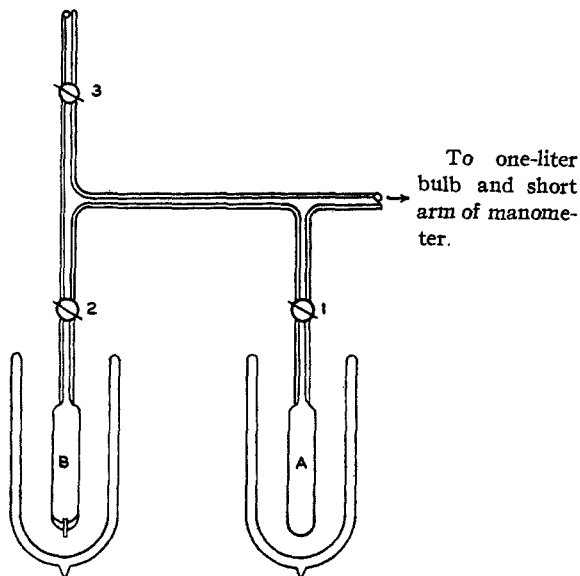


Fig. 1.—A, condensing bulb for ammonia in line; B, condensing bulb for ammonia in 1-liter bulb.

results. The corresponding numbers at one-third of an atmosphere, as shown in Table II, were fourteen and four.

TABLE I
DENSITY OF AMMONIA AT $\frac{2}{3}$ ATM.

As determined with 5-liter Pyrex bulb				As determined with 1-liter Jena glass bulb (baked)			
Expt.	Approx. res. press., mm.	Density, g./l.	Average	Expt.	Approx. res. press., mm.	Density, g./l.	Average
16	0.0	0.51190		120	0.0	0.511590	
24	.0	.51191		121	.0	.511631	
32	.0	.51201	0.51194				
13	5.0	.51199		122	.0	.511609	
14	5.0	.51172		123	.0	.511613	
28	5.0	.51185	.51186				
15	10.0	.51179		124	40.0	.511586	
30	10.0	.51189	.51184	125	40.0	.511599	0.511605
31	15.0	.51166	.51166				

The results obtained with the five-liter Pyrex bulb at the lower pressures varied as did those at one atmosphere, *i. e.*, the densities decreased with increasing residual pressures. However, the limiting values were still higher than the densities as later determined with the one-liter bulb which

TABLE II
DENSITY OF AMMONIA AT $\frac{1}{3}$ ATM.

As determined with 5-liter Pyrex bulb				As determined with 1-liter Jena glass bulb (baked)			
Expt.	Approx. res. press., mm.	Density, g./l.	Average	Expt.	Approx. res. press., mm.	Density, g./l.	Average
18	0.0	0.25492		126	0.0	0.254559	
20	.0	.25471		127	.0	.254575	
57	.0	.25487					
58	.0	.25482		128	.0	.254598	
59	.0	.25474	0.25482	129	.0	.254576	0.254576
17	5.0	.25480					
26	5.0	.25467					
35	5.0	.25473	.25473				
19	10.0	.25478					
34	10.0	.25466					
63	10.0	.25470					
64	10.0	.25467	.25470				
65	20.0	.25471					
66	20.0	.25470	.25471				

had been baked before being used. Experiments Nos. 120–125 are divided into three groups of two each. In Nos. 120–121 the adsorbed ammonia in the line was pumped out under conditions as previously described. In Nos. 122–123 it was condensed in bulb A. Finally in Nos. 124–125 the residual pressure instead of being zero was about 40.0 mm., the adsorbed ammonia in the line being removed by pumping. It is significant that the six density values obtained under these varying conditions agree to within slightly less than five parts in fifty thousand. The close agreement between the first four and the last two determinations also seemed to prove conclusively that the absorption effect in the one-liter bulb, as well as in the line, had been eliminated completely. The density at two-thirds of an atmosphere was accordingly considered to be 0.51161 (≈ 0.00001).

Four density determinations at one-third of an atmosphere, Nos. 126–129, corresponding to Nos. 120–123 at two-thirds, resulted in a mean value of 0.25458 (≈ 0.00001).

Discussion of Results

In the paper by Dietrichson, Bircher and O'Brien it was pointed out that the density of ammonia could be calculated by means of an equation of the form

$$d_n = \frac{m}{v_1} = \frac{M(1 + \bar{\lambda})}{RT_0}$$

Correspondingly, by using experimentally determined densities, it is possible to compute molecular weights and from these in turn atomic weights. Obviously in doing this it is necessary to assign values to R , T_0 and λ . Molecular and atomic weights obtained in this manner will

therefore be significant only in so far as these constants, or quantities equivalent to them, are accurately known.

The limitations involved in the above method of determining atomic weights, which was originally proposed by Guye, have been admirably set forth in a paper by Baxter⁴ entitled "The Significance of the Density of Hydrogen Bromide with Reference to the Atomic Weight of Bromine." Attention is called especially to the uncertainty with regard to λ which he defines by the equation $p_0v_0/p_1v_1 = 1 + \lambda$, *i. e.*, the ratio of the pressure-volume product at zero pressure to that at one atmosphere, and computed from density data at different pressures. As Baxter states, however, various procedures have been adopted in extrapolating for the p_0v_0 products with consequent variations in λ . The two that are discussed are referred to as a "method of secondary differences" and an "algebraic method." In effect these are the same mathematically in that both assume a quadratic rather than a linear relation.

In his own subsequent determinations of the density of oxygen, nitrogen and the rare gases, Baxter⁵ obtains the p_0v_0/p_1v_1 ratios at two or three pressures below one atmosphere and then, by using the method of first differences, extrapolates each of these to zero pressure for $p_0v_0/p_1v_1 = 1 + \lambda'$.⁶ Moles in his papers on ammonia follows essentially the same procedure except that he finds d/p , or $1/pv$, for each pressure and applies the method of first differences to these values in order to get a limiting density, d_0/p_0 or $1/p_0v_0$. Using his notation, the equation is written in the form, $L_0/L_{Lim.} = 1 + \lambda''$, which corresponds to

$$\frac{1/p_1v_1}{1/p_0v_0} = \frac{d_1/p_1}{d_0/p_0} = \frac{L_0}{L_{Lim.}} = 1 + \lambda''$$

In this equation p_1 , v_1 and d_1 represent the values of these quantities at one atmosphere and p_0 , v_0 and d_0 the limiting values at zero pressure. Moles, as does Baxter, calculates a separate λ to correspond to each pressure at which density determinations have been made and takes the mean as his final value. As will be illustrated in Table III, treatment of the same set of density data by these two operations does not give identical results. That is what one would expect if the pressure-volume product, p_0v_0 or d/p , is a quadratic rather than a linear function of the pressure.

The situation with regard to the method of differences as applied to determining the value of λ can possibly best be illustrated by means of curves, Fig. 2, showing the variations of p_0v_0 and of d/p with p for ammonia. If plotted on a sufficiently large scale it is found that, in general, there is a curvature. It necessarily follows that extrapolation to zero pressure

(4) Baxter, *THIS JOURNAL*, **44**, 595 (1922).

(5) Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **10**, 479 (1924); **11**, 231 (1925); **12**, 20 (1926); **13**, 699 (1926); **14**, 50 (1928); **15**, 441 (1929).

(6) For the sake of differentiation, the λ as defined by Baxter will be designated as λ' , that by Moles as λ'' and that by the authors of this paper as λ''' .

TABLE III
ATOMIC WEIGHTS FROM GAS DENSITIES

Density	NH ₃ D. B. O. and D. O. R.	NH ₃ M. and B.
g./l. 1 atm.	0.77126	0.77169
$\frac{2}{3}$ atm.	.51161	.51181
$\frac{1}{2}$ atm.		.38293
$\frac{1}{3}$ atm.	.25458	.25461
$pv = a + bp + cp^2$	$pv = 1315.403 - 17.767p - 1.054p^2$	$pv = 1316.025 - 20.452p + 0.192p^2$
$p_0v_0/p_1v_1 = 1 + \lambda'$	1.014901	1.01540
$M = v_0d_n/(1 + \lambda')$	17.0335	17.0346
At. wt. N	14.0101	14.0112
$L_0/L_{Lim.} = 1 + \lambda''$	1.015003	1.01552
$M = v_0d_n/1 + \lambda''$	17.0318	17.0323
At. wt. N	14.0084	14.0089
$(1/pv)_{p \rightarrow 0} [\partial(pv)/\partial p]_T = \lambda'''$	0.015109	0.015249
$M = v_0d_n/(1 + \lambda''')$	17.0300	17.0372
At. wt. N	14.0066	14.0138

becomes increasingly uncertain the greater this effect. In the case of ammonia the curvature is quite pronounced, especially with the data as reported in this paper.

The authors feel that the coefficient of deviation from Boyle's law should be defined as $(\frac{1}{pv})_{p \rightarrow 0} [\frac{\partial(pv)}{\partial p}]_T = \lambda'''$. An evaluation of λ when so defined naturally necessitates an equation of state in terms of p and v . Using the method of least squares, the densities being weighted in proportion to pressures, the following equation per gram of ammonia at 0° was developed.

$$pv = 1315.403 - 17.767p - 1.054p^2$$

For purposes of comparison a similar equation was developed for Moles and Batuecas' data on ammonia. Table III presents a summary of the various computations involved. The value for v_0 as obtained by Baxter and Starkweather in their work on oxygen was used throughout.

$$v_0 = RT_0 = \frac{M(1 + \lambda)}{d_n} = \frac{32 \times 1.00092}{1.42897} = 22.4144$$

It will be noted that the atomic weight of nitrogen, that of hydrogen being assumed to be 1.0078, was found to show considerable variation. It appears therefore that the gas density method for the determination of atomic weights cannot at present be considered as reliable as that based on gravimetric analyses, not because of insufficient accuracy as regards the gas densities, but rather because of uncertainties in connection with λ , R and T_0 (also $v_0 = RT_0$). This conclusion is in accordance with that stated by Baxter in his paper on hydrogen bromide.⁴

In view of the above considerations it seems therefore more profitable at present to use density data for the purpose of determining more accu-

rately the value of R , the gas constant and v_0 , the limiting molal volume at 0° . This can be done by considering that the constant, a , in the linear or quadratic equation is equivalent to RT_0/M . In other words, $pv = RT_0/M + bp$ or $pv = RT_0/M + bp + cp^2$. An evaluation of R and v_0 requires accordingly the constant, a , as obtained from the equation of

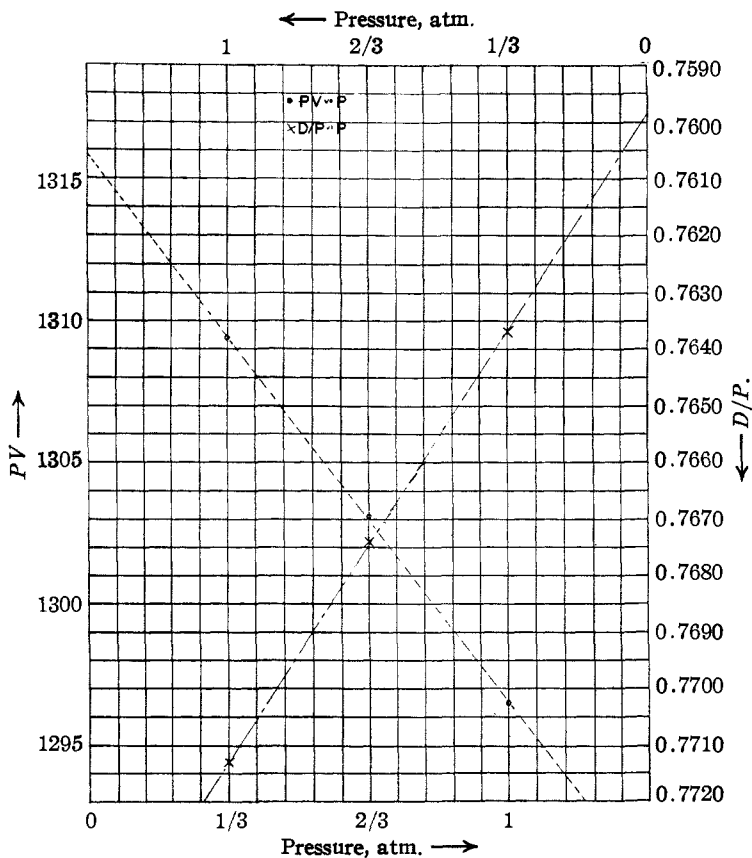


Fig. 2.

state and assumed values for T_0 and the atomic weights involved. Table IV presents a summary of the calculations that were made with the two forms of equation. The constants, a , b and c , were in each case determined as previously explained, *i. e.*, by using the method of least squares, the densities being weighted in proportion to the pressures. The following tabulation indicates the number of density determinations involved.

Pressures in atm.	1	2/3	1/2	1/3
NH ₃ (D. B. and O. and D. O. and R.)	4	6		4
NH ₃ (M. and B.)	39	17	18	23

A comparison of R and v_0 fails to show agreement in the case of either form of equation. In view of the known curvature of ammonia in plotting pv or d/p against p one would expect the best results with the second power equation. However, it must be kept in mind that a determination of these constants by the equation of state method involves again a more or less uncertain extrapolation. In other words, it is assumed that the curvature between zero and one-third of an atmosphere will be the same as that between one-third and one atmosphere. Density data at still lower pressures would obviously be helpful in settling this question. Also, additional data on other gases are needed. Among these carbon dioxide is of particular interest since the atomic weight of carbon has been determined with such accuracy and, furthermore, the proportion of carbon to oxygen is small. Density determinations of carbon dioxide by the method described in this and the preceding paper are now under way.

The value of R given in the "International Critical Tables," 82.06 cc. atm., is that derived by Keyes⁷ on the basis of equations of state involving the densities of hydrogen, nitrogen, oxygen and carbon dioxide. The accuracy, however, is probably not greater than one part in two thousand. About the same time Henning⁸ reported a value of 82.04 (± 0.03).

In connection with the above, attention may be called to the fact that the second derivative of the equation derived from the authors' data is -2.108 , the curvature therefore being convex upward in the range from zero to one atmosphere. This is in agreement with the compressibility isotherms at 25 and 50° as reported by Meyers and Jessup,⁹ who obtained data extending into the low pressure region.

TABLE IV

THE GAS CONSTANT, R , AND THE LIMITING MOLAL VOLUME, v_0

	$pv = a + bp$		$a = RT_0/M$		$T_0 = 273.16^\circ\text{K.}$			
	a	b	M	R		$v_0 = RT_0$		
NH ₃ (D. B. and O. and D. O. and R.)	1316.484	-20.066	17.0312	82.081		22,421.3		
NH ₃ (M. and B.)	1315.940	-20.177	17.0312	82.047		22,412.0		
	$pv = a + bp + cp^2$			$a = RT_0/M$		$T = 273.16^\circ\text{K.}$		
	a	b	c	M	R	$v_0 = RT_0$		
NH ₃ (D. B. and O. and D. O. and R.)	1315.403	-17.767	-1.054	17.0312	82.015	22,403.2		
NH ₃ (M. and B.)	1316.025	-20.452	+0.192	17.0312	82.053	22,413.6		

The equations for these are as follows

$$pv_{25^\circ} = 1436.16 - 14.700p - 0.220p^2$$

$$pv_{50^\circ} = 1552.86 - 10.314p - 0.193p^2$$

The densities obtained by Moles and Batuecas result in a curvature in the opposite direction.

(7) F. G. Keyes, *Am. Soc. Refrig. Eng. J.*, 8, 505 (1922).

(8) F. Henning, *Z. Physik*, 6, 69 (1921).

(9) Meyers and Jessup, *Refrig. Eng.*, 11, 345 (1925).

Summary

1. The density of ammonia at two-thirds and one-third of an atmosphere has been determined and found to be 0.51161 (± 0.00001) and 0.25458 (± 0.00001).

2. The gas density method for the determination of atomic weights has been discussed.

3. The gas constant, R , and the limiting molal volume, v_0 , have been computed by means of linear and quadratic equations of state developed on the basis of density data for ammonia as determined by the authors and by Moles and Batuecas.

CAMBRIDGE, MASSACHUSETTS

RECEIVED MAY 20, 1932
PUBLISHED JANUARY 11, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. I. Conductance as Influenced by the Dielectric Constant of the Solvent Medium¹

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I. Introduction

While solutions of electrolytes in solvents of high and of intermediate dielectric constant have been studied extensively, similar solutions in solvents of very low dielectric constant have not been investigated systematically. We know only that such solutions generally are poor conductors and that the equivalent conductance falls rapidly with decreasing concentration.

In addition to a number of isolated observations on the conductance of solutions in benzene,³ and several series of measurements relating to the conductance of complex compounds in various solvents at relatively high concentrations,⁴ the literature includes two important papers by Walden and his co-workers, who investigated⁵ the conductance of a variety of *salts* in benzene, ether, carbon tetrachloride and similar solvents. According to Walden's measurements, the equivalent conductance of solu-

(1) This paper comprises a part of the subject matter of a thesis submitted by Raymond M. Fuoss in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

(2) Jesse Metcalf Fellow in Chemistry in Brown University, 1931-1932.

(3) Kablukov, *Z. physik. Chem.*, **4**, 430 (1889), hydrogen chloride in ether and in benzene; Cady and Lichtenwalter, *This Journal*, **35**, 1434 (1913); Cady and Baldwin, *ibid.*, **43**, 646 (1921), heavy metal soaps in benzene; La Mer and Downes, *ibid.*, **53**, 888 (1931), conductimetric titrations in benzene; Hill, *ibid.*, **44**, 1164 (1922), silver perchlorate in benzene.

(4) Complexes in ether, Plotnikov, *Z. physik. Chem.*, **57**, 502 (1906); Ussanowitsch, *ibid.*, **124**, 427 (1926); Bruns, *Z. anorg. allgem. Chem.*, **163**, 120 (1927); complexes in bromine, Plotnikov, *Z. physik. Chem.*, **116**, 111 (1925); Finkelstein, *ibid.*, **121**, 46 (1926); Plotnikov and Jakobson, *ibid.*, **138**, 235 (1928); Plotnikov and Kudra, *ibid.*, **145**, 625 (1929); complexes in toluene, xylene, and benzene, Plotnikov and Jakobson, *ibid.*, **147**, 227 (1930); Jakobson, *ibid.*, **118**, 31 (1925); Rabinowitch, *ibid.*, **132**, 83 (1928).

(5) Walden, *Bull. Acad. Imp. Sci. St. Pet.*, **7**, 934 (1913); Walden, *Z. physik. Chem.*, **147**, 1 (1930).