THE VALENCE OF OXYGEN, SULPHUR, NITROGEN AND PHOSPHORUS DETERMINED FROM THE MOLECULAR COHESION

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1. The valence of oxygen

In my paper on the relation of molecular cohesion to molecular weight and valence,¹ in which the number of valences were computed from the value "*a*" of van der Waals' equation, I considered oxygen to be bivalent except in the case of oxygen gas. The question of the quadrivalence of oxygen was not taken up, because I wished to get the main point of the connection of valence and cohesion well established before discussing particulars. But as it is believed by many that oxygen is at times quadrivalent and as this possibility has such an important bearing on theories of association and solubility and, indeed, on the ionizing powers of water, and is also full of importance in physiology, it is interesting to examine the oxygen compounds of that table for evidence in favor of tetravalence.

One atom of oxygen is supposed by Stieglitz, Armstrong, and Goldschmidt² to be quadrivalent in the esters. In the first table, therefore, I have incorporated the results of a determination from the molecular cohesion by the usual formula: $n = a^{3/2} \times 3.2 \times 10^5 / (\text{mol. wt.})$, of the total number of valences per molecule, and compared it with the number of valences computed if one oxygen is quadrivalent. I have taken only those esters whose critical data were recently very carefully determined by Young. All of these esters associate a little at low temperatures, but their vapors are normal for some degrees below the critical temperature, except possibly that of methyl formate.

¹ Mathews: Jour. Phys. Chem., **17**, 181 (1913).

² Zeit. Elektrochemie, **10**, 221 (1904).

TABLE I

Substance	Formula	"a"	Theoretical No. of valences. One oxygen quadrivalent	Number of valences det. from cohesion
Ethyl acetate	$C_4H_8O_2$	0.04076	30	29.9
Ethyl formate	$C_3H_6O_2$	0.03122	24	23.9
Ethyl propionate	$C_5H_{10}O_2$	0.05088	36	36.0
Methyl acetate	$C_3H_6O_2$	0.03206	24	24.8
Methyl butyrate	$C_5H_{10}O_2$	0.05082	36	35.9
Methyl formate	$C_2H_4O_2$	0.02371	18	19.5
Methyl isobutyrate	$C_5H_{10}O_2$	0.04882	36	33.8
Methyl propionate	$C_4H_8O_2$	0.03968	30	28.8
Propyl acetate	$C_5H_{10}O_2$	0.05149	36	36.7
Propyl formate	$C_4H_8O_2$	0.04086	30	29.7

From Table 1 it is clear that the number of valences computed from the molecular cohesion is very close to the theoretical number, if one of the oxygen atoms is quadrivalent. The only cases in which fewer valences were found were methyl isobutyrate and methyl propionate. In the former, the computation of "a" may not be exactly right as elsewhere pointed out, the isocompounds always giving a value for "a" a little low as compared with the normal. It is, of course, possible that in them the oxygen is bivalent.

Table 2 contains some other oxygen compounds which associate and may be supposed on that account to have quadrivalent oxygen.

In Table 2 the alcohols probably associate somewhat at the critical temperature and acetic acid also; the number of valences, given in the table as computed, were computed with the normal molecular weight and they are, accordingly, too many. It is impossible to determine the total number of valences per molecule by this method for these substances until the average molecular weight has been independently determined at the critical temperature. Of the other substances: acetone, anisol, phenetol, nitrobenzene, acetic anhydride, ethyl diacetate and methyl propyl ketone appear to have tetravalent oxygen. The method, however, is not

TABLE 2

Substance	Formula	"a"	Number of valences computed; one oxygen quadrivalent	No. of valences found
Acetone	C_3H_6O	0.02459	22	21.3
Ethyl alcohol	C_2H_6O	0.02395	18	25.8 (Assoc.)
Anisol	C_7H_8O	0.05645	40	39.8
Methyl alcohol	CH_4O	0.01895	12	26.0 (Assoc.)
Phenetol	$C_8H_{10}O$	0.07009	46	48.7
Propyl alcohol	C_3H_8O	0.03250	24	31.3 (Assoc.)
Acetic acid	$C_2H_4O_2$	0.03504	18	34.9 (Assoc.)
Nitrobenzene	$C_6H_5NO_2$	0.05968	38	37.9
Acetic anhydride	$C_4H_6O_3$	0.04442	30	29.3
Ethyl diacetate	$C_6H_{10}O_3$	0.06668	42	42.4
Methyl propyl ketone	$C_5H_{10}O$	0.04437	34	34.8
m-Cresol	C_7H_8O	0.06254	40	46.0 (Assoc.)

sufficiently accurate to enable this conclusion to be drawn without reservation. The critical data of some of these substances have not been determined with entire accuracy and it is possible, in some, that a very small amount of association may occur at the critical temperature and such association would have the effect of making uncertain the valence determination. With these reservations, however, this method undoubtedly supports the view that oxygen may be tetravalent, and particularly that one atom is tetravalent in the esters.

The method shows oxygen to be bivalent in ether, sulfur dioxide, carbon dioxide and one of the oxygen atoms of the esters.

In oxygen gas, carbon monoxide and nitric oxide, NO , the oxygen is monovalent, if computed from the cohesion. The maximum number of valences in a molecule of oxygen found by this method was two. It must be confessed that it seems unlikely that oxygen is monovalent in the gaseous form, but the critical data are accurately determined and if this method of determining valence is reliable, as it appears to be, there is no escaping the conclusion. The critical data of carbon monoxide should be redetermined, but from those

accepted only two valences can be found in the molecule. Nitric oxide has always been a puzzle, since the oxygen is monovalent, or the nitrogen bivalent. The cohesion shows that there are only two valences, which again means that the oxygen and nitrogen are monovalent.¹

From its cohesion, then, oxygen appears to be either monovalent, bivalent, or tetravalent.

2. Sulfur

Sulfur is generally supposed to be bivalent, but at times to open up two or four residual valences. So far I have not found any compounds with bivalent sulfur, except probably carbonyl sulfide, when the valence is computed from the cohesion. All the sulfur compounds have either quadrivalent or hexavalent sulfur, if the valence is determined by this method. Even sulfuretted hydrogen is no exception to this statement. Table 3 contains the results.

TABLE 3—THE VALENCE OF SUBSTANCES CONTAINING SULFUR

Substance	Formula	"a"	Valences per mol.		Valences per mol. by cohesion
			S = 6	S = 4	
Hydrogen sulfide	H ₂ S	0.00890	8	6	7.9
Mercaptane	C ₂ H ₆ S	0.02497	20	18	20.4
Thiophene	C ₄ H ₄ S	0.04130	26	24	32.0 (Assoc.)
Sulfur dioxide	SO ₂	0.01349	10	8	7.8
Carbon bisulfide	CS ₂	0.02316	16	12	14.8
Sulfuryl chloride	SO ₂ Cl ₂	0.04382	16	14	14.1
Thionyl chloride	SOCl ₂	0.03110	14	12	14.8

¹ A very interesting fact which may be cited in support of the view that oxygen in these three gases is in a state different from the ordinary, and, hence, possibly monovalent, is the following: Oxygen gas and nitric oxide are strongly paramagnetic, and carbon monoxide is far more paramagnetic, or rather far less diamagnetic, than carbon dioxide which contains more oxygen. In all other compounds oxygen is diamagnetic. It is clear that the oxygen in the three gases which this method shows to contain monovalent oxygen has magnetic properties different from oxygen in other oxygen compounds. This fact has not hitherto been explicable. The following figures showing the para- or diamagnetism of different gases I have taken from Auerbach's article on Magnetism in the *Handbuch der Physik*, 5, 274 (1908).

O₂ NO CO Air C₂H₄ CH₄ CO₂ N₂O N₂ H₂
 +4.83; +1.60; -0.009; 1; -0.068; -0.063; -0.033; -0.018; -0.015; -0.002(?)

From Table 2 it appears that sulfur is quadrivalent in sulfur dioxide and sulfuryl chloride; hexavalent in sulfuretted hydrogen, carbon bisulphide, mercaptane, thionyl chloride and probably in thiophene. It is probably bivalent in carbonyl sulphide, but the critical data are uncertain. These results are in agreement with the general idea of the valence of sulfur except in the case of sulfuretted hydrogen, mercaptane, and carbon bisulfide. Thiophene probably associates a little at the critical temperature so that the valence computation is uncertain.

3. Nitrogen

Nitrogen is generally supposed to be either mono-, tri- or pentavalent. The cohesion method supports this conclusion. Nitric oxide has been a stumbling block. The results are given in Table 4.

TABLE 4—NUMBER OF VALENCES PER MOLECULE OF NITROGEN COMPOUNDS

Substance	Formula	"a"	Number of valences found from cohesion	Number computed		
				N = 1	N = 3	N = 5
Nitrogen	N ₂	0.0032808	2.0	2	6	10
Nitrous oxide	N ₂ O	0.009465	6.2	4	8	
Nitric oxide	NO	0.002570	1.4	2	4	
Nitric dioxide	NO ₂	0.01119	7.6		7	9
Ammonia	NH ₃	0.00844	13.5		6	8 (Assoc.)
Methyl amine	CH ₃ N	0.01521	17.9		12	14 (Assoc.)
Dimethyl amine	C ₂ H ₇ N	0.01922	17.5		18	20
Trimethyl amine	C ₃ H ₉ N	0.02594	22.7		24	26
Diethyl amine	C ₄ H ₁₁ N	0.03625	27.9		30	
Triethyl amine	C ₆ H ₁₅ N	0.05415	39.9		42	
Propyl amine	C ₃ H ₉ N	0.02729	24.5		24	
Dipropyl amine	C ₆ H ₁₅ N	0.05835	51.2		52	
Aniline	C ₆ H ₇ N	0.05157	37.2		34	36
Dimethyl- <i>o</i> -toluidine	C ₉ H ₁₃ N	0.08187	51.2		52	54

From the table it appears that nitrogen in nitrogen gas is monovalent. It appears to be also monovalent in nitrous and nitric oxide. Two formulas may be written for nitrous oxide with a total valence of six, *i. e.*, N—O—N or N—N=O.

I think the former, with some of the molecule having quadri-valent oxygen, is perhaps the more probable. I have taken the highest possible value of "*a*" for nitrous oxide. In nitric oxide two valences per molecule are the most that can be assigned by this method. This would mean that both elements were monovalent, but as there is other evidence that oxygen is univalent in its elemental form, this formula is not entirely improbable. The valence of nitrogen in nitric dioxide is quite uncertain. In the amines there can be hardly a doubt that it is trivalent, or at times pentavalent with two free valences on the nitrogen. This is the case in ammonia and methyl amine, both of which associate. All of the critical data of the amines were determined by Vincent and Chappuis and I believe their figures are uniformly a little too low. In aniline the nitrogen appears to be pentavalent, but some association occurs. The results are not, then, very satisfactory for these compounds, but they indicate very clearly, however, that nitrogen is either monovalent, trivalent, or pentavalent, as it is supposed to be.

4. *Phosphorus*

I have found but a single phosphorus compound in which the critical data have been directly determined, although one or two other cases were reported in my paper on the valence of chlorine, in which the critical data had been computed from the surface tension.

In phosphoretted hydrogen the phosphorus is apparently pentavalent, having two free valences. "*a*" is given by Leduc and Sacerdote as 0.00939 and from this the valence of 8.6 is computed. Were the phosphorus pentavalent the total number of valences would be eight. It might be, however, that the phosphorus was heptavalent, but only a few of the molecules had the two pairs of reserve valences open at the same instant. In the chlorine compounds it appeared that the phosphorus was probably heptavalent. I think the only certain conclusion is that the valence is greater than three.

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