Infra-Red Absorption Spectra of Eleven Arsine Sulphides from 15 to 30 μ

The As—S Stretching Frequency

By Ralph A. Zingaro, Raymond E. McGlothin and Richard M. Hedges

Dept. of Chemistry, Agricultural and Mechanical College of Texas

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The infra-red spectra of eleven arsine sulphides and some of their corresponding arsines have been measured in the potassium bromide and caesium bromide region. Included were eight trialkyl-derivatives, the triphenyl-derivative and two monosubstituted derivatives of trivalent arsenic. Molecular-weight determinations indicate that monoalkylarsine sulphides are strongly associated in solution.

Assignment of the As—S stretching frequency can be made with confidence for the seven straight-chain trialkyl derivatives. The spectra of the phenyl- and cyclohexyl-derivatives are more complicated and these spectra are discussed in relation to those observed for the monosubstituted benzenes.

A discussion of mass and chemical effects on the As—S stretching frequency is included.

We have been unable to locate any information on the location of the As—S stretching frequency. We have been involved, during the past several years in a study of the interaction of group 5 oxides and chalcogenides with halogens. The effect of halogen complexing on the M—X stretching frequency, where M is a group 5 atom and X a group 6 atom, has been of considerable interest to us. Because of this effort we have had to synthesize a representative number of arsine sulphides. The examination of these compounds, together with a preliminary calculation using empirical formulae, has enabled us to establish, with a high level of confidence, the location and nature of the As—S stretching frequency in molecules of the general formula, $R_1R_2R_3AsS$, where the R's are organic substituents.

EXPERIMENTAL

ARSINES AND ARSINE SULPHIDES

With the exception of the four new derivatives described below, the method of preparation of these compounds and their physical properties are described in previous publications.[1-4] The preparation involved condensation of an arsenic trihalide with the appropriate Grignard reagent, except for the butyl derivatives where n-butyllithium in heptane was used. Following acid hydrolysis, the layers were separated and the ether layer was dried over sodium sulphate. The ether was removed by distillation and the arsines were then separated by vacuum distillation. All of the arsines were clear, colourless liquids.

The sulphides were prepared by refluxing an alcoholic solution of the arsine with sulphur, evaporation of the alcohol, and then recrystallization, or vacuum distillation of the arsine sulphide.

The physical constants of the previously reported arsines and their sulphides, used in this study were as follows: trimethylarsine, b.p. 49·5° under nitrogen pressure; trimethylarsine sulphide, m.p. 183°; triethylarsine, b.p. 137°; triethylarsine sulphide, m.p. 119-120°; tricyclohexylarsine separated as a very viscous syrup following evaporation of ether after hydrolysis of cyclohexylmagnesium bromide-phosphorus trichloride reaction was not further purified; tri-n-propylarsine, b.p. 59-60° at 4·4 mm; tri-n-propylarsine sulphide, m.p. 40-40·5° from ethanol, extremely hygroscopic; tri-n-butylarsine, b.p. 76-78° at 1·1 mm; tri-n-butylarsine sulphide b.p. 137-138·5° at 0·40 mm; tri-n-amylarsine, b.p. 131-133° at 3·3 mm; triphenylarsine, recrystallized from ethanol, m.p. 59-60°; triphenylarsine sulphide, m.p. 160°; methylarsine sulphide, m.p. 109-111°; phenylarsine sulphide, m.p. 152°.

TRI-n-AMYLARSINE SULPHIDE

The reaction of tri-n-amylarsine with a slight excess of sulphur followed by vacuum distillation of the reaction mixture gives a clear, colourless liquid, b.p. 147-149° at 0·70 mm, n_D^{25} 1·5093. (Anal., calc. for $C_{15}H_{33}AsS$: C, 56·23; H, 10·38; S, 10·01; found: C, 56·51; H, 10·26; S, 9·88.)

TRICYCLOHEXYLARSINE SULPHIDE

Under a nitrogen atmosphere, 15·2 g (0·05 mole) of tricyclohexylarsine in 200 ml ethanol is refluxed with 1·61 g (0·05 mole) of sulphur for 30 min. The hot solution is filtered and on cooling yields 15 g (89 %) of colourless crystals of tricyclohexylarsine sulphide, m.p. 178·5-180°. Molecular weight, calc., 356·4; found, by vapour pressure method, 356·4. (Anal., calc. for $C_{18}H_{33}AsS$: C, 60·65; H, 9·33; S, 9·00; found: C, 60·58; H, 10·24; S, 9·00.

METHYLDIETHYLARSINE SULPHIDE

The arsine was prepared by the addition of ethylmagnesium bromide to methyldiiodoarsine [5] in ether. The sulphide was prepared from 7·4 g (0·05 mole) of the crude arsine and 1·3 g (0·05 mole) of sulphur in 50 ml ethanol refluxed under nitrogen for an hour. The hot solution was filtered to remove unreacted sulphur and the crude product was recrystallized from ethanol. Methyldiethylarsine sulphide was obtained in the form of colourless crystals, m.p. 96-98°. (Anal. calc. for $C_5H_{13}AsS$: C, 33·34; H, 7·27; S, 17·80; found: C, 33·12; H, 7·21; S, 17·61.)

METHYLDI-n-BUTYLARSINE SULPHIDE

The arsine was prepared by the addition of excess n-butyllithium to methyldichloroarsine in heptane in a dry nitrogen atmosphere at 0°. After hydrolysis, separation of the layers and evaporation of the heptane, 89·4 g (0·4 mole) of crude methyldi-n-butylarsine was fused with 12·8 g (0·4 mole) of sulphur under nitrogen. The sulphur was taken up rapidly and the mixture was vacuum distilled. Methyldi-n-butylarsine sulphide was obtained as a colourless liquid, b.p. 140·5-141·5° at 0·75 mm which froze to a solid, m.p. 41°. (Anal. calc. for $C_9H_{21}AsS$: C, 45·75; H, 9·12; S, 13·57; found: C, 45·76; H, 9·12; S, 13·27.

METHYLDIPHENYLARSINE

The addition of excess phenylmagnesium bromide to methyldiiodoarsine, followed by ammonium chloride hydrolysis, separation and drying of the layers gave a pale yellow liquid, b.p. 133-136° at 0·1 mm, identified as methyldiphenylarsine. (Anal. calc. for $C_{13}H_{13}As$: C, 63·95; H, 5·36; As, 30·69; found: C, 63·93; H, 5·35; As, 30·43.

Methyldiphenylarsine was not converted to the sulphide because of the remarkable lack of activity of this compound toward sulphur. Attempted fusion of this compound with sulphur followed by vacuum distillation always led to recovery of the unreacted arsine.

SPECTRA

All spectra were measured on a Perkin-Elmer model 21 for which both KBr and CsBr prisms were available. Samples were run as pure liquids, Nujol mulls, or, depending upon their solubilities, as solutions in iso-octane, carbon disulphide, or chloroform.

RESULTS AND DISCUSSION

The spectra of the trialkylarsines are remarkably similar and well defined in the 15-30 μ region. All have two or three well-defined absorptions in the 15-18 μ region and are transparent throughout the remainder of the KBr—CsBr region. The trialkylarsine sulphides show absorption which is identical to that of the corresponding arsine except that they are all characterized by an intense additional absorption in the 20-22 μ region. Such a comparison is demonstrated in fig. 1 and the absorption frequencies of a series of trialkylarsine and their corresponding sulphides are given in table 1. In table 2 are listed the frequencies observed for some monoalkylarsines and for cyclohexyl- and phenyl-substituted derivatives.

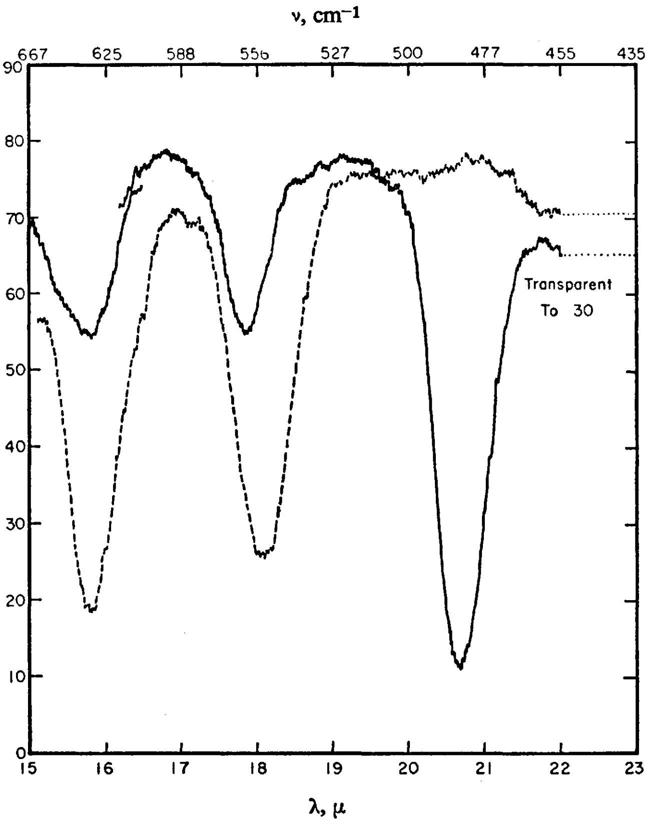


FIG. 1.—The infra-red spectrum of pure, liquid tris(n-butyl)arsine (0·001 cm KBr cell) is shown by the dashed curve; that of a 5 % solution of pure tris(n-butyl)arsine sulphide in iso-octane (0·044 cm CsBr cell) is shown by the solid line.

Using the equation of Gordy[6] we can estimate the force constant of an isolated As—S bond. The expression used is the following

$$k = 1{\cdot}67N[X_aX_b/d^2]^{\frac{3}{4}}+0{\cdot}30, \tag{1}$$

where k is the force constant $\times 10^{-5}$ dynes/cm, N is the bond order, X is the electronegativity of the atoms and d is the internuclear distance in Å. For a " pure " double bond, $N = 2$ and, from Pauling,[7] $X_{\mathrm{As}} = 2{\cdot}0$ and $X_{\mathrm{S}} = 2{\cdot}5$ and $d_{\mathrm{As=S}} = 2{\cdot}05$ Å, we calculate $k = 4{\cdot}098 \times 10^5$ dynes/cm.

TABLE 1.—OBSERVED FREQUENCIES IN cm^{-1} OF TRIALKYLARSINES AND ARSINE SULPHIDES IN 670-330 cm^{-1} REGION

substituents	physical state	R_3As		$R_3As—S$			
		As—C (aliphatic)[a]		As—C (aliphatic)[a]			As—S[b]
$(CH_3)_3$	solid			615	582		472·8
	soln. 4 % in $CHCl_3$						472·8
$(CH_3)(C_2H_5)_2$	solid			605	581[c]	561	466·2
	soln. 5 % in CS_2						477·3
$(CH_3)(n\text{-}C_4H_9)_2$	solid			648[c]	597	583[c]	466·2
	soln. 5 % in iso-octane			636	588	557[c]	{485·9 484·3}[d]
$(C_2H_5)_3$	liquid	604	557				
	solid			583		{558 555}	458·7
	soln. 5 % in CS_2			583		553	476·2
$(n\text{-}C_3H_7)_3$	liquid	628	546				
	liquid			634		559	477·3
	soln. 7 % in iso-octane			634[e]		559	{487·1 485·4}
$(n\text{-}C_4H_9)_3$	liquid	628	553	633		570	478·5
	soln. 5 % in iso-octane			633		570	486·6
$(n\text{-}C_5H_{11})_3$	liquid	654	557				
	liquid			636		563	479·6
	soln. 6 % in iso-octane			636		563	484·7

[a] assignment is probable, but tentative. [b] all As—S absorptions are very strong. [c] band is of weak intensity; other bands are medium to medium-strong in intensity relative to As—S. [d] all bracketed pairs are doublets. [e] poorly resolved.

TABLE 2.—OBSERVED FREQUENCIES IN 670-330 cm^{-1} REGION IN MONOSUBSTITUTED ARSINE SULPHIDES AND IN ARSINES AND ARSINE SULPHIDES BEARING PHENYL- AND CYCLOHEXYL-GROUPS

compound	physical state										
$C_6H_5AsH_2$	liquid	opaque up to 650 cm^{-1}	615 (shoulder)				433*a*				
C_6H_5AsS	solid	*b*				465		395	373		
$(C_6H_5)_3As$	soln. 5 % in iso-octane		622 (weak)			465					313 (wide)
$(C_6H_5)_3AsS$	soln. 5 % in $CHCl_3$	*b*			490	470				337,	333
$(C_6H_5)_3AsS$	solid				490 487	465 456				345,	327 (medium)
$(C_6H_{11})_3As$	liquid	*b*	636 (medium)		493		437 (medium)				
							434} 433} (poorly resolved)			372	
$(C_6H_{11})_3AsS$	soln. 5 % in CS_2	transparent to ~500 cm^{-1}			493	476	431			330,	399 (wide, medium)
$(C_6H_{11})_3AsS$	solid	transparent to ~500 cm^{-1}			493	476					
$(CH_3)AsS$				565							

[a] unless otherwise indicated, bands are of strong intensity. [b] strong absorption at 667 cm^{-1} becoming more transparent with increasing wavelength. Frequency maximum is probably located at somewhat higher frequency.

For a "pure" single bond, i.e., $\overset{+}{\mathrm{As}}$—$\overset{-}{\mathrm{S}}$, $d_{\overset{+}{\mathrm{As}}-\overset{-}{\mathrm{S}}} = 2{\cdot}25$ Å and $k = 1{\cdot}823 \times 10^5$ dynes/cm. From the fundamental equation which relates the frequency of a harmonic oscillator to its force constant and the reduced mass, viz.,

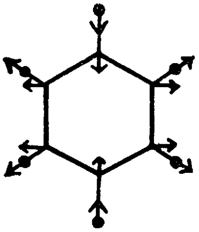
$$\tilde{\nu}\,(\mathrm{cm}^{-1}) = 1307\,(k/\mu)^{\frac{1}{2}}, \qquad (2)$$

we calculate $\tilde{\nu}_{\mathrm{As=S}} = 555\ \mathrm{cm}^{-1}$ or 18 μ and $\tilde{\nu}_{\overset{+}{\mathrm{As}}-\overset{-}{\mathrm{S}}} = 372\ \mathrm{cm}^{-1}$ or 26·9 μ.

Inasmuch as the fundamental As—S stretching frequency is not "isolated" in the molecules actually studied, i.e., the vibrational energy is not entirely concentrated in this bond, it is quite proper [8] to establish the region of occurrence of this frequency in the manner just described. It is reasonable to expect the nature of bond in the molecules to be between these extremes, depending upon the nature of the substituent groups.

Although it is not strictly correct to establish the location of the As—S stretching frequency by virtue of the fact that a given frequency is observed in the $R_1R_2R_3AsS$ compound but not in the $R_1R_2R_3As$ compound, the experimental observations indicate that the R_1As, R_2As and R_3As stretching frequencies (tentatively assigned to the 15-18 μ region) remain essentially unchanged throughout the $R_1R_2R_3As$ and $R_1R_2R_3As$—S pairs of molecules. Furthermore, the relative intensity of the new band found in arsine sulphides as compared with the free arsine analogue and the surprisingly narrow range over which the new band is found in addition to its location relative to that predicted from the empirical equations makes it possible to assign the As—S stretching frequency with a high level of confidence for the trialkyl derivative (table 1). We thus assign the intense band located in the range from 470-490 cm^{-1} as the fundamental As—S stretching frequency in that series of trialkylarsine sulphides listed in table 1.

There is a small shift to a slightly higher frequency in the location of this vibration for the dissolved compounds as compared with those in the pure state. This suggests a higher bond order. In a few cases, e.g., tripropyl- and methylbis(n-butyl)arsine sulphides, the vibration is observed as a doublet. It is probable that this splitting would be observable in all cases with optics possessing adequate resolution. A similar case of splitting of the P—O frequency in $(Me_3O)PO$ has been attributed [9] to splitting of the *E* vibrations into two bands since this molecule possesses only approximate C_{3v} symmetry. Similar observations have been made on the P—O and P—S vibrations [10-13] but all of these investigators have suggested that the splitting is due primarily to intermolecular association with the formation of different aggregates. We believe that a similar explanation is correct for the arsine sulphides. The various possibilities for association have been discussed in the references just given and the present data do not suggest alternate explanations for such splitting.



(I)

The assignment of the As—S stretching frequency for the phenyl- and cyclohexyl-derivatives cannot be made with the high level of confidence as that for the trialkyl compounds. This is due primarily to the presence of additional absorptions in

KBr—CsBr region, which, at least for phenyl derivatives we attribute, according to Plyler,[14] to mode (I). This mode is infra-red inactive in benzene, but becomes infra-red active in substituted benzenes. This vibration is, of course, mass sensitive, and is observed [14] in the region from 521-448 cm^{-1}, going to lower frequencies with increasing mass. In the sequence methyl-, fluoro, ethyl-, bromo, iodo benzene this frequency is observed in the region from 519-448 cm^{-1}. We would, therefore, expect to find similar absorptions for the phenyl-bearing arsines and arsine sulphides. It is probable that the strong vibrations observed at 433 cm^{-1} (phenylarsine hydride) and at lower frequencies for the molecules bearing phenyl substituents, may be logically attributed to this type of mode.

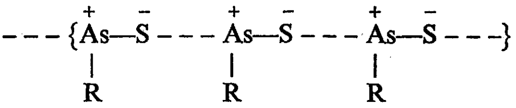
For triphenylarsine sulphide the intense absorption at 490 cm^{-1} (split in the solid) can be assigned with reasonable certainty to the As—S stretching vibration. The absorption at 465 cm^{-1} also characteristic of the phenyl-bearing compounds (but not observed for phenylarsine hydride) is undoubtedly also due to one of the modes discussed by Plyler.[14] The As—S assignment is further justified by the strong intensity of the band, and its location at a frequency higher than that observed for any of the alkyl compounds. Electronegative phenyl groups will, of course, increase the As—S bond order and the frequency will rise.

Tricyclohexylarsine and its sulphide also demonstrate considerably more complex absorption in the longer wavelength region than do the corresponding simple alkyls. This is undoubtedly due to skeletal ring vibrations and other modes similar to those just discussed for the phenyl-derivatives. Inasmuch as the cyclohexyl group should exhibit an inductive effect comparable with, or greater than, that of the alkyl substituents, we would not expect the As—S fundamental to be displaced to any great degree in this molecule in comparison with alkyl compounds. We thus assign the band at 476 cm^{-1} as the As—S fundamental in tricyclohexylarsine sulphide. We assume that the vibrations on either side of this, at 493 cm^{-1} and 437 cm^{-1}, which are found also in the arsine, are not displaced upon the addition of the sulphur atom.

The assignment of the As—S fundamental for the monosubstituted arsine sulphides, CH_3AsS and C_6H_5AsS, is least certain. These molecules are of different symmetry than the trisubstituted derivatives and there are, of course, additional electrons available which would contribute to the As—S bonding. These lines of reasoning suggest that the strong absorption at 565 cm^{-1} should be assigned to the As—S fundamental in methylarsine sulphide. This value is not unusually high since a combination of the inductive effect of the methyl group and the available unused 4*p* electrons of the arsenic atom would make for a higher As—S bond order than can be expected for any of the other molecules. For phenylarsine sulphide, the only reasonable assignment seems to be the 465 cm^{-1} absorption, but it is difficult to understand why it should occur at a lower frequency than that for the triphenyl compound. This assignment must be considered tentative. The 395 cm^{-1} and 373 cm^{-1} values are much too low.

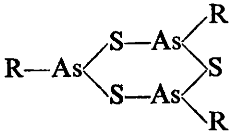
Molecular-weight determinations in bromomethane (using the vapour pressure method) give the values 728 for phenylarsine sulphide and 394 for methylarsine sulphide. For an aggregate indicated by the general formulation $\{RAsS\}_n$ these values give $n = 4{\cdot}00$ for the phenyl derivative and $n = 3{\cdot}23$ for the methyl derivative.

Association probable occurs via the $\overset{+}{As}—\overset{-}{S}$ dipole, i.e.,



$$---\{\underset{\substack{|\\R}}{\overset{+}{As}}—\overset{-}{S}---\underset{\substack{|\\R}}{\overset{+}{As}}—\overset{-}{S}---\underset{\substack{|\\R}}{\overset{+}{As}}—\overset{-}{S}---\}$$

with ring structures of the type



also being possible. Elucidation of this problem will require the use of other experimental techniques.

Using the values just reported, the dependency of the As—S frequency on the masses of the substituent groups is shown in fig. 2. It is to be noted from fig. 2 that the As—S frequency depends almost entirely upon the mass of substituent

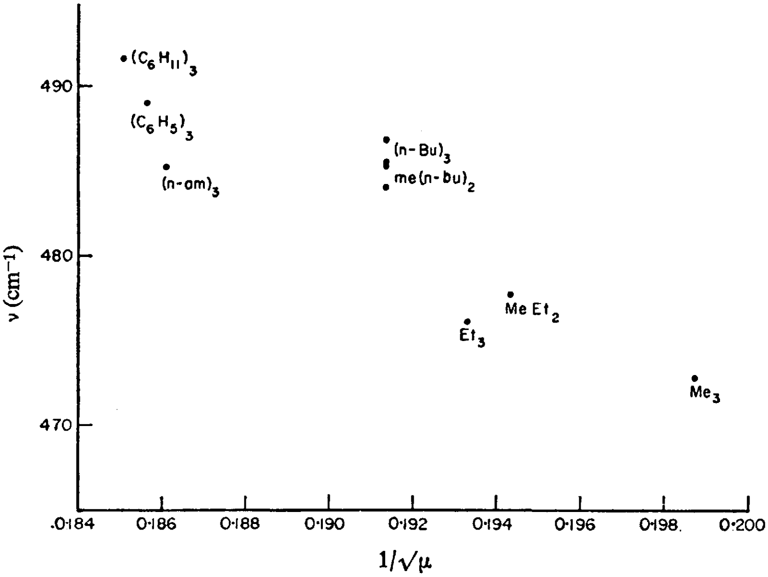


FIG. 2.—The dependency of the fundamental As—S stretching frequency on the mass of the substituents on the arsenic atom. The reduced mass μ is that of the group R_3As—. The frequencies used are those observed in solution so that the physical state is comparable.

groups *provided that we are dealing with* As—C *bonds only.* The As—S force constant appears to remain essentially constant among this series of molecules. It is probable that the electronegativity of groups attached to the arsenic atom play an important role in determining the position of the As—S bond. Experimental verification of this fact must await the synthesis of arsine sulphides bearing highly electronegative (or electropositive) substituents, such as the trihaloarsine sulphides. We are unaware of the existence of such molecules at the present time.

One fact of interest concerns the transparency of the triphenyl- and monophenyl-derivatives in the 600-700 cm^{-1} region where the symmetric and asymmetric aliphatic C—As frequencies should occur. These molecules have strong absorption at the limit of the KBr region which indicates that phenyl-As vibrations are to be found at higher frequencies than the aliphatic C—As frequencies. This is supported by the observations of Daasch and Smith [15] who report aliphatic C—P vibrations to be found at frequencies up to several hundred wave numbers lower than the aromatic-P vibrations.

The As—S stretching frequency in the trialkylarsine sulphides is well established, and it is worthwhile to estimate the force constant from eqn. (1). Since the range over which this frequency is located is quite narrow over the entire range of aliphatics from trimethyl, total mass 45, $\tilde{\nu}_{As—S} = 472{\cdot}8\ cm^{-1}$ to tricyclohexyl, total mass 249, $\tilde{\nu}_{As—S} = 476\ cm^{-1}$, the normal As—S vibration appears to behave as a characteristic group vibration and the value of μ, the reduced mass, will be taken as that of the atom pair, As—S. Using an average value of $\tilde{\nu}_{As—S} = 480\ cm^{-1}$ gives $k_{As—S} = 3{\cdot}03 \times 10^5$ dynes/cm.

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[1] Krause and von Grosse, *Die Chemie der Metall-Organischen Verbindungen* (Edward Bros. Inc., Ann Arbor, Mich., 1943), p. 450-585.
[2] Roberts, Turner and Bury, *J. Chem. Soc.*, 1926, 1443.
[3] Dyke, Davies and Jones, *J. Chem. Soc.*, 1931, 185.
[4] Jones, Dyke, Davies, Griffiths and Webb, *J. Chem. Soc.*, 1932, 2284.
[5] Millar, Heaney, Heinekey and Fernelius, *Inorganic Syntheses* (McGraw-Hill Book Co., Inc., New York, N.Y., 1960), vol. 6, p. 113.
[6] Gordy, *J. Chem. Physics*, 1946, **14**, 305.
[7] Pauling, *Nature of the Chemical Bond* (Cornell Univ. Press, 1960), chap 3 and 7.
[8] Gore, *Disc. Faraday Soc.*, 1950, **9**, 138.
[9] Baudler, *Z. Elektrochem.*, 1955, **59**, 193.
[10] Goubeau and Berger, *Z. anorg. Chem.*, 1960, **304**, 147.
[11] Hooge and Christen, *Rec. trav. chim.*, 1958, **77**, 911.
[12] MacIvor, Grant and Hubley, *Can. J. Chem.*, 1956, **34**, 1611.
[13] Zingaro and Hedges, *J. Physic. Chem.*, 1961, **65**, 1132.
[14] Plyler, *Disc. Faraday Soc.*, 1950, **9**, 100.
[15] Daasch and Smith, *Anal. Chem.*, 1951, **23**, 853.