evidence, indicate the over-all activation energy for this process to be of the order of 48,000 calories, if it is assumed to be a first order reaction, for the temperature change from 70 to 75°. This process does not appear to be repressed at higher temperatures and proceeds readily at 99°.

The second process, which can take place only after the first process has occurred, will proceed at temperatures below that at which the first is initiated. The second process is accompanied by a marked increase in electrophoretic mobility over that of the native protein or that of the product of the first process. It is also accompanied by a further increase (probably unlimited) in particle weight but no marked further increase in frictional ratio. This second process, at temperatures of 70° and below and in phosphate buffer of *p*H 6.9, ionic strength 0.1, proceeds with a constant activation energy of about 28,000 calories and a temperature coefficient between 60 and 70° of about 3.6 ($Q_{10} = 3.6$). It accurately follows the concentration–time characteristics of a second order reaction. Above a temperature of 75° this process is markedly repressed as the temperature is increased until at 99° it does not take place at all. Increase in *p*H or decrease in ionic strength of the solution, in which the heat denaturation is carried out, depress the rate of this reaction. The postulate is offered that this process is influenced to a marked extent by the electrokinetic potential of the particles of the primary denatured protein. As yet, there is no evidence that the first process of denaturation is so affected.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1017]

On Arsenomethane

BY JURG WASER AND VERNER SCHOMAKER

The question of the structure of arseno compounds, the compounds of arsenic of composition analogous to the azo compounds, has been investigated in the past mainly by molecular weight determinations in solutions[1] and to some extent by studies of their chemical reactions.[2] The chemical considerations appear to have been dominated by the notion that arseno compounds have the structure R—As=As—R, analogous to that of azo compounds R—N=N—R, and it seems that the majority of organic chemical opinion accepts this idea. It is unlikely that arseno compounds actually have the doubly bonded structure, however, for the molecular weight determinations have generally indicated a degree of polymerization, *n* in the formula $(RAs)_n$, of about four or five, and always greater than two. Moreover, the double bond structure violates the general rule, which probably has no important exceptions, that only first row elements (of the periodic table) form what have to be regarded as multiple covalent bonds. For arsenic the remarkable structure of skutterudite,[3] $CoAs_3$ or $Co_4(As_4)_3$, with its four-membered, singly-bonded arsenic rings, provides an example of the working of this rule insofar as the structure might have been expected to involve —As=As— groups. The arsine oxides $(RAsO)_n$ also are subject to confusion in this respect, for they appear to be generally regarded as monomeric although the same arguments apply to them as to the arseno compounds, and some of them have been shown by molecular weight determinations[1] to be certainly polymeric.

It was hoped that on the basis of an electron diffraction study a definite structure could be assigned to arsenomethane[4] $(CH_3As)_n$ that would establish the correct formula for this particular arseno compound. It proved impossible to determine the structure unambiguously on the basis of the diffraction data alone, although the double bond structure could be definitely eliminated. Vapor density measurements were therefore undertaken for the information they might provide regarding the degree of polymerization of arsenomethane in the vapor state. The present study also includes an investigation of some other properties of arsenomethane.

Preparation and Properties

Arsenomethane was prepared by the action of hypophosphorous acid on sodium methylarsenate[5] which had been prepared by refluxing an aqueous solution of sodium arsenite with methyl iodide. The arsenomethane was distilled in a high vacuum and was stored in vacuum-sealed ampoules. An analysis indicated C, 13.22, and H, 3.34 (calculated for $AsCH_3$: C, 13.15; H, 3.36).

Arsenomethane exists in two modifications, a light yellow oil and a brick red to dark brown solid modification, the latter being the more stable at room temperature. If the yellow oil was left standing in contact with air for a period of weeks a red solid slowly formed, which contained less

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[1] *E. g.*, F. F. Blicke and F. D. Smith, THIS JOURNAL, **52**, 2946 (1930).

[2] For references see *e. g.*, G. W. Raiziss and J. L. Gavron, "Organic Arsenical Compounds," Reinhold Publ. Corp., New York, N. Y., 1923.

[3] I. Oftedal, *Z. Krist.*, **66**, 517 (1928); *cf.* also *Z. Krist.*, "Strukturbericht," 1931, p. 232.

[4] V. Auger, *Compt. rend.*, **138**, 1705 (1904); W. M. Dehn, *Am. Chem. J.*, **33**, 120 (1905); **35**, 8 (1906), **40**, 109 (1908); E. V. Zappi, *Bull. soc. chim.*, (4) **23**, 322 (1918); F. A. Paneth, *Trans. Faraday Soc.*, **30**, 179 (1934); *J. Chem. Soc.*, 366 (1935); W. Steinkopf and H. Dudek, *Ber.*, **61**, 1906 (1928); A. Valeur and P. Gailliot, *Compt. rend.*, **185**, 956 (1927).

[5] C. S. Palmer and A. B. Scott, THIS JOURNAL, **50**, 536 (1928).

than 13.15% C and 3.36% H, and gave an X-ray powder pattern essentially identical with the pattern produced by pure arsenious oxide.

Addition of traces of hydrochloric acid induced rapid transformation of the yellow oil to a solid modification of dark color, which contained 13.43% C and 3.35% H. X-Ray powder patterns of this $(AsCH_3)_n$ modification will be discussed later.

Various experiments were carried out with samples of the yellow modification sealed in glass ampoules. Cooling in liquid air or Dry Ice and alcohol causes the yellow oil to solidify into a pale yellow glass, which on warming to about 10° melts partially and, after some minutes, usually crystallizes. The melting point of the crystals is 12°. The oil can be supercooled considerably; for example, it stayed liquid for hours at −10°. At 4° the crystals, which are yellow, turn orange within an hour and very dark red within a day, but a liquid sample, on the other hand, shows no change in two weeks.

This behavior of the crystals seems strange. It may possibly be due to a small amount of impurity and incomplete crystallization, so as to leave a solution containing the impurity in high concentration. If in this higher concentration the impurity (possibly a small amount of the red form in solution which precipitates on concentration; see below) induces the transformation, the behavior described above may result. Some support for this explanation is given by the observation that the crystals always appeared somewhat moist. On melting, the orange or dark red crystals produced a turbid mixture of yellow oil with very fine red particles in suspension, which could be filtered off. The red material so obtained yielded the same X-ray diffraction pattern as did the red modification obtained from the yellow oil with traces of hydrogen chloride. When the above mentioned turbid mixture was heated for an hour or more at 100°, the conversion of the yellow oil to the red modification proceeded substantially, while heating of the yellow oil at 100° for even a longer time produced no change. No evident change was effected by heating the yellow oil at 100° in ampoules which also contained some of the red modification clinging to the walls or in the form of visible particles suspended in the liquid. It appears that the conversion of the yellow to the red form is catalyzed by the red form and that the surface available is of importance. It was not investigated whether inert particles, such as finely ground glass, would produce the same effect.

Heating in ampoules at 180–205° causes the red modification or mixtures of the yellow and red modification to revert to the yellow oil, which then remains yellow for weeks at room temperature. At 180–205° the yellow modification is thus the stable form, while at 100° and below the red modification is the more stable. No attempt was made to find a definite transition temperature, however, perhaps none exists, for it is not even certain whether the red modification is a uniform substance. Heating at 205–215° causes irreversible change; bubbles appear, a precipitate forms and the color darkens, turning first red and then black. No attempt was made to identify the decomposition products. Whenever the yellow modification contained some of these decomposition products at room temperature, considerable change to the red form occurred within a few hours.

Molecular Weight Determinations

Various cryoscopic and ebullioscopic molecular weight determinations on arsenomethane have been reported. Measurements of the freezing point depression in benzene by Auger[4] were corrected by Steinkopf, Schmidt and Smie[6] by taking into account the depression due to dissolved carbon dioxide, which was used to provide an inert atmosphere, and a value $n \approx 5$ in $(AsCH_3)_n$ was reported. The latter authors themselves carried out cryoscopic and ebullioscopic determinations in nitrobenzene and benzene and found $n \approx 5$. A slight trend to higher values of the molecular weight with increasing concentration was ascribed to oxidation of the arsenomethane. This explanation would seem to be based on a misconception, unless the authors tacitly assumed that oxidation is accompanied by polymerization or precipitation. Possibly an equilibrium between different states of association manifests itself in the data. Measurements of the boiling point elevation in benzene and carbon disulfide were made by Palmer and Scott[5] who found $n \approx 5$. Their data are not sufficient to show whether or not an equilibrium is at hand between different association states.

Some rough determinations of the density of the vapor of the yellow modification were undertaken in the present investigation. The measurements were made at temperatures between 170 and 270° at several concentrations. The pressures were too low to be measured reliably, but the results do provide a strong indication of a temperature and concentration dependent equilibrium between different association states, possibly involving a pentamer and lower association states. For example, with a concentration of 0.20 g./liter at 200°, n is approximately 5, whereas at 0.11 g./liter and 270°, n is approximately 3. The pressures of the saturated vapor indicate a heat of vaporization of about 15 kcal./mole and a boiling point at 10 mm. of about 190°.

X-Ray Diffraction Study

Samples of the dark-colored modification obtained by subjecting the yellow form of arsenomethane to a trace of hydrochloric acid and samples obtained from crystals of the yellow form in the way described in the preceding section yielded the same powder pattern with Cu K_α radiation. The estimated intensities and the positions of the thirty-two lines on the diffraction photographs (Table I) were used in the computation of the radial distribution function.[7]

$$rD(r) = c \sum_i \frac{\sin 2\theta_i \exp(-1.5h^2(\theta_i))}{1 + \cos^2 2\theta_i} I(\theta_i) \sin(2\pi h(\theta_i)r)$$

Here $h = 2 \sin \theta/\lambda$, λ denotes the wave length, 2θ is the angle of reflection and the exponential

TABLE I

h	I	h	I	h	I
0.15	100	0.48	2	0.75	5
.19	7	.49	5	.77	2
.22	7	.52	23	.79	1
.25	4	.56	28	.83	2
.29	25	.58	2	.87	3
.32	20	.61	7	.94	7
.35	37	.64	3	1.01	5
.38	32	.66	7	1.04	7
.40	7	.68	1	1.12	5
.44	20	.70	1	1.16	5
.46	20	.73	1		

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(6) W. Steinkopf, S. Schmidt and P. Smie, *Ber.*, **59**, 1463 (1926).

(7) V. Schomaker, to be published.

function is a convergence factor. The $I(\theta_i)$ represent the integrated intensities of segments of equal heights of the powder lines on the film, which in the experiment have been arranged cylindrically about the powder sample.

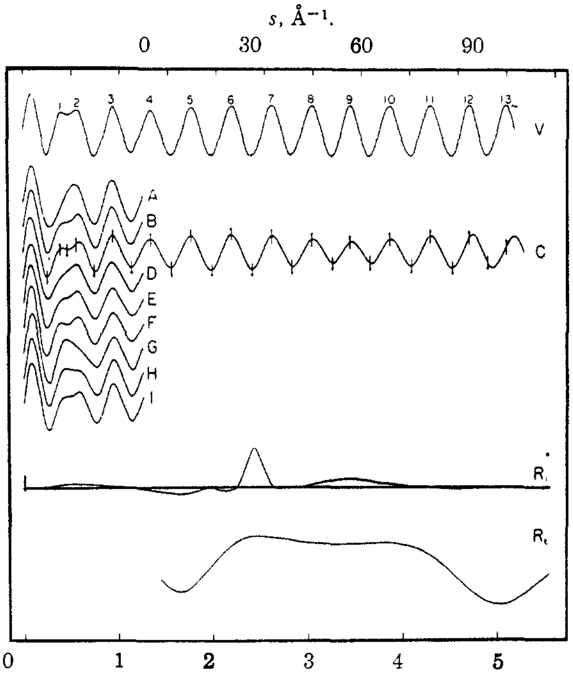

Fig. 1.

The resulting function $rD(r)$ is represented by curve R_2 in Fig. 1. The broad feature[8] between 1.6 and 5 Å., corresponding to intramolecular interatomic distances and the shortest intermolecular distances, is unfortunately not well resolved. It, however, appears to contain a peak at 2.4 Å. corresponding to an As–As single bond (covalent radius, sum 2.42 Å.[9]). The remainder of this feature undoubtedly represents mainly the van der Waals contacts, which should occur at about 4 Å., the van der Waals radii for both arsenic and methyl being 2.0 Å.,[10] and the non-bonded $\underset{\diagdown\text{As}\diagup}{\text{As}\cdots\cdots\text{As}}$ distances, which should be somewhat shorter.

No detailed conclusion about the structure of the dark colored form of arsenomethane can be drawn from this analysis of the radial distribution function. The important item, however, is the peak at 2.4 Å. which indicates that, whatever kinds of molecules are present in this modification, a predominant number of them contain As–As single bonds.

Electron Diffraction Investigation

An electron diffraction investigation was carried out with vapor from a sample of the yellow modification heated to about 200°. The diffraction pictures were made in the usual way[11] with electron wave length 0.0609 Å. and film distances of about 10 and 20 cm. The residues in the high temperature nozzle were found to consist of unchanged arsenomethane, and the material which accumulated in the trap of the electron diffraction apparatus appeared to be the red modification of arsenomethane. These facts make it improbable that decomposition occurred to any marked extent, and indicate that the diffraction pictures are characteristic of arsenomethane and not of any derived product (such as cacodyl, which might be expected to give a diffraction pattern more or less similar to the one here obtained).

From the appearance of the rings and their measured positions the visual curve V (Fig. 1) was drawn. Except for the inner doublet and minor characteristics of the other features out to about $q = 50$, the pictures are like those of a diatomic molecule.

The visual curve V was used in the evaluation of the radial distribution function

$$rD(r) = \int_0^{s_{\max}} \sin(sr)I(s)\exp(-as^2)\mathrm{d}s$$

by the approximation[12]

$$rD(s) \approx \sum_i \sin\left(\frac{\pi}{10} q_i r\right) V(q_i)\exp(-a'q_i^2)$$

with $q_i = 1,2 \cdots 100$, $\left(q = \frac{10}{\pi}s\right)$ and $\exp - a'(100)^2 = 0.03$.

The resulting curve (R_1 in Fig. 1) has a main peak at 2.42 Å., the As–As covalent single bond radius sum, a smaller peak at 1.98 Å. which apparently represents As–C single bonds, the sum of the covalent radii being just 1.98 Å,[10] and a broad feature centered at about 3.44 Å. This feature must represent the non-bonded As · · · As distances and so corresponds to an average bond angle of about 90°, but it must also include some of the non-bonded As · · · C distances. Assuming a C–H distance of 1.08 Å. and a tetrahedral configuration of the CH_3 groups, the shortest As · · · H distances would be expected at 2.55 Å., within the region covered by the peak at 2.42 Å.

Assuming that one kind of molecule is predominantly responsible for the electron diffraction pattern, the following speculations may be made to explain this pattern. The ratio of the area of the peak at 2.42 Å. to the area of the broad peak at 3.44 Å. is 1.2, a value which suggests that each arsenic atom has the same number of unbonded neighbors at approximately 3.5 Å. as it has bonded neighbors at 2.42 Å. This would be

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(8) A radial distribution function for which the exponential convergence factor was omitted was calculated also. The result showed slightly improved resolution, but also the effects of breaking off the Fourier series at a point where the coefficients were still large.

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 2nd ed., Ithaca, N. Y., 1940, p. 165.

(10) Ref. 9, p. 189.

(11) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(12) R. A. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942).

the case for a five membered ring of arsenic atoms (the most plausible example; the same would hold, *e. g.*, for a cube) with each arsenic atom singly bonded to a methyl and its two ring neighbors, but would not be true for the square, which at first sight is suggested by the observed bond angle. However, the only pentagon with all sides and angles equal is the regular pentagon with angles of 108°, so that a pentagon with equal sides and average angle of 90° cannot be planar and must have several different diagonal distances and correspondingly various bond angles. The breadth of the peak at 3.44 Å. is most easily explained by the notion that the potential barriers in question are low, so that the molecule would carry out large-amplitude librations which would affect the cross-ring distances about its various equilibrium configurations (probably with frequent transitions from one to another); but even a rigid molecule might suffice if the bond angles had values such that the cross-ring distances were evenly distributed through the region covered by the 3.44 Å. peak. At any rate, the five-membered ring is unique in this respect; tetragons, hexagons, heptagons, etc., can be constructed with equal sides and equal angles for a whole range of possible angles and not just for a certain definite angle, and molecules having any of these structures may be expected to have equal ring bond angles unless the ring-bonds are not all fundamentally alike. The breadth of the peak at 3.44 Å. therefore provides further support for the assumption of a pentagonal configuration of arsenomethane, since it can be naturally explained with this model.

A number of theoretical intensity functions were calculated according to the formula[13]

$$I'(q) = k \sum_{ij} \frac{Z_iZ_j}{r_{ij}} \sin\left(\frac{\pi}{10} q r_{ij}\right)$$

for several variants of the model suggested by the radial distribution function. The As–As, As–C and As · · · H distances were kept unvaried at 2.42, 1.98 and 2.55 Å., respectively. The same number of As–As bonds as As–C bonds, and three times as many As · · · H distances being assumed. The contributions to $I'(q)$ of the shorter non-bonded As · · · As and As · · · C distances were introduced together as wide temperature distributions with positions r_0, half-widths w, and areas a, close to those suggested by the radial distribution function, and the various longer non-bonded distances depending on more than one bond angle were neglected, as is reasonable. Curves calculated in this way for the values of these parameters listed in Table II are shown in Fig. 1. The significance of the parameter a used in Table II is such that a = 2, for example, means twice as many As · · · As distances as As–As distances. Only one of the curves (C) is shown beyond q = 25 in Fig. 1 since all the others are identical with it in this region. Curves C, F and I reproduce features 1 and 2 correctly and are generally satisfactory, while all the others are unsatisfactory. Table III shows the observed positions $q_{obs.}$ of the various features of the diffraction pattern, the values $q_{calcd.}$ calculated for model C and the ratios between them. Curve A is of special interest because it represents a model which, like a four-ring, has only half as many As · · · As distances as As–As distances. The calculated intensity curves thus confirm the analysis of the radial distribution curve in indicating that immediately after evaporation the arsenomethane molecule may well be a pentamer having irregular non-planar pentagonal structure with average As–As–As bond angle of 90°. The observation[5,6] that arsenomethane seems to exist as a pentamer in solution provides additional support for this suggestion, which, if correct, shows that the establishment of the

TABLE II

Curve	w, Å.	a	r_0, Å.
A	0.35	0.5	3.44
B	.35	1.0	3.44
C	.35	1.2	3.44
D	.52	1.0	3.44
E	.52	1.3	3.44
F	.52	1.7	3.44
G	.35	1.0	3.20
H	.35	1.0	3.32
I	.35	1.0	3.40

TABLE III

Max.	Min.	$q_{calcd.}$	$q_{obs.}$	$q_{calcd.}/q_{obs.}$
	1	5.1	4.9	(1.041)
1		8.3	8.0	(1.037)
	2	9.7	10.0	(0.970)
2		11.8	12.1	(0.975)
	3	15.2	15.4	0.987
3		18.7	18.7	1.000
	4	22.5	22.5	1.000
4		26.5	26.5	1.000
	5	30.6	30.8	0.994
5		34.8	34.8	1.000
	6	39.0	39.2	0.995
6		43.1	43.3	0.995
	7	47.5	47.5	1.000
7		51.7	51.6	1.002
	8	55.9	55.7	1.004
8		60.0	59.8	1.003
	9	64.0	64.1	0.998
9		68.2	67.7	1.007
	10	72.1	71.8	1.004
10		76.1	75.9	1.003
	11	80.4	80.8	0.995
11		84.5	84.4	1.001
	12	88.9	88.9	1.000
12		93.1	92.4	1.007
	13	97.4	96.2	(1.012)
13		101.5	100.1	(1.014)
			Av.	1.000
			a. d.	0.004

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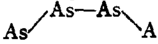
[13] The effective scattering power of arsenic (here represented by an effective atomic number) was taken to be five times stronger than that of carbon and twenty-five times stronger than that of hydrogen.

equilibrium between different states of association observed in the vapor density measurements must be a relatively slow process.

Granted that the As–As–As bond angle of about 90° in arsenomethane is determined by a tendency of arsenic to form bonds at about this angle in such a compound,[14] it is difficult to see why a distorted five-membered ring structure should occur rather than a simple four-membered ring, as might be suggested by the example of skutterudite. Perhaps the significant point is that in the five-membered ring each arsenic atom has altogether five heavy atom neighbors, including two arsenic atoms that are not bonded to it in the ordinary sense, whereas in the four-membered ring structure it would have only one such non-bonded arsenic atom neighbor. If the direct interactions between non-bonded arsenic atoms tend to stabilize the molecule, then this difference between the two structures would make the five-membered ring the more stable; one might say that in the arsenomethane molecule the tricovalent arsenic atoms had a certain tendency to quinquevalency. The van der Waals distance appropriate to the interactions between non-bonded arsenic atoms is certainly less[15] than the standard van der Waals distance[10] 4.0 Å., but because the lines connecting non-bonded atoms make relatively large angles (~45°) with the adjoining bonds the difference is perhaps not great. In any event the observed As · · · As distance, being only 3.4 Å., suggests that there should be strong interaction between the non-bonded arsenic atoms with a resultant energy of interaction that might be positive, negative, or even zero depending upon what is actually the appropriate van der Waals distance for this situation and on the extent of incipient covalent bond formation. On the other hand, it is possible that the five-membered ring structure would be favored because of the existence of a potential energy (analogous to that in ethane[16]) related to internal rotation about the As–As bonds and unfavorable to the *cis* orientation. In the five-membered ring structure with average bond angle of about 90° most or all of the  $As\diagup^{As-As}\diagdown As$ groups are twisted far out of the *cis* configuration whereas in the four-membered ring structure they would be held at least quite close to the *cis* orientation.

The definite conclusions from the electron diffraction experiments may be summarized, however, by the statements that the molecules of arsenomethane vapor have As–As bonds of length 2.42 ± 0.02 Å., As–C bonds of length 1.98 ± 0.04 Å., and an exceptionally wide range of As–As–As bond angles averaging about 90°. The distances show that the bonds are single bonds, being in exact agreement with the covalent radius[9] sums. They may be compared with the values 2.44 Å., 2.46 Å. and 2.50 Å. reported[9,3] for As–As in As_4, $Co_4(As_4)_3$ and metallic arsenic, and with the distance 1.98 Å. found[9] for $As(CH_3)_3$.

Acknowledgment.—We are indebted to Professor L. Pauling for suggesting this study and pointing out its interest in connection with the chemistry of other arsenic compounds. We also wish to thank Mr. J. Renno, Jr., for assistance in the preparation of the compound, Dr. G. Oppenheimer for the microanalyses, and Mr. W. Shand, Jr., for help with the vapor density measurements.

Summary

A study has been made of some of the properties of arsenomethane, which occurs both in a yellow liquid form and a red solid modification, and particularly of the transformation between the two forms. Vapor density measurements strongly indicate the existence in the vapor of an equilibrium between different states of association, which, under the conditions of the experiments, leads to degrees of polymerization of $(AsCH_3)_n$ ranging from about three to about five. X-Ray powder photographs of the red solid revealed the presence of singly bonded arsenic. An electron diffraction study of the vapor led to an As–As distance of 2.42 ± 0.02 Å., an As–C distance of 1.98 ± 0.04 Å. and an average angle As–As–As of 90°. A puckered five-membered ring of arsenic atoms is compatible with the diffraction pattern. Both the diffraction studies, which led to the value for the As–As distance that would be expected for single bonds and the vapor density measurements rule out the azomethane-like structure $CH_3—As=As—CH_3$.

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[14] Observed bond angles for trivalent arsenic range from 60° in As_4 through 90° in $Co_4(As_4)_3$, 96° in $As(CH_3)_3$ and 97° in metallic arsenic to about 100° in the trihalides: *cf.* ref. 9, p. 80.

[15] Ref. 9, p. 193.

[16] J. D. Kemp and K. S. Pitzer, THIS JOURNAL, **59**, 276 (1937).