Ring Frequencies.—In the isolated D_{3h} cyanuric acid molecule one should expect four ring stretching frequencies, of which two, of symmetry class A_1' and A_2', are inactive in the infrared. Of the two doubly degenerate E' pairs one should probably be quite active and the other only moderately so. If the ring were stripped of peripheral atoms this vibration would become virtually inactive due to the near equality of the masses of nitrogen and carbon atoms. In the reduced symmetry of the crystal, the vibration derived from A_1' might become weakly active, but the A_2' mode should scarcely be expected to gain significant activity. As was mentioned above, the splitting of the E' pairs might well be rather small.

We ascribe the single intense and unpolarized band at 1470 cm.$^{-1}$ to one of these pairs and the perpendicularly polarized narrow doublet at 1050 and 1065 cm.$^{-1}$ to the other. None of these bands shows appreciable shift on deuteration. The last mentioned doublet, however, appears to suffer significant decrease in intensity on deuterium substitution, though our observations are very qualitative. This is perhaps not surprising since for reasons mentioned above one of the E' pairs may owe a considerable portion of its moderate intensity to the small motions of peripheral atoms, the amplitudes of which may be significantly affected by deuteration.

Out of Plane Vibrations.—From their relatively high intensity in the powder spectrum as compared with that of the (101) crystal, it is probable that 807 and 765 cm.$^{-1}$ correspond to out of plane vibrations. The former appears to shift to 570 cm.$^{-1}$ on deuteration (807/570 = 1.4), while the latter

both increases in intensity and shifts slightly to higher frequency. The small frequency shift could be accounted for by an interaction between the two vibrations. Presumably the only out of plane fundamentals which could lie in this region are the N–H and C=O bendings. We tentatively ascribe 807 cm.$^{-1}$ to the former, though the frequency seems rather low for this mode, and 765 to the latter. In a previous investigation[8] the out of plane C=O bend in urea was ascribed to 790 cm.$^{-1}$.

Conclusion

As has been shown above the infrared observations are compatible with a previous X-ray structure determination as far as the presence of an essentially symmetrical ring is concerned; but are in disagreement in regard to the periphery of the cyanuric acid molecule. In contradiction to the X-ray determination it appears very probable that all C=O distances are nearly equal and are not greater than the 1.25 Å. found in diketopiperazine. The N–H···O hydrogen bond distances, on the other hand, are probably not all equal. The stronger bond appears to be formed in the case when the C=O and N···O directions make an angle of around 124° with each other. The bonds parallel to the b axis must be lengthened corresponding to the shortening of the C=O distance, and the N–H···O distance is probably not less than 2.87 Å.

The Microwave Spectrum and Structure of Methylene Fluoride[1]

BY DAVID R. LIDE, JR.[2]

The K-band microwave spectrum of the slightly asymmetric rotor CH_2F_2 has been recorded and analyzed. Many of the lines appear as close doublets which are due to asymmetry splitting of levels which would be degenerate in the limiting symmetric rotor. The rotational constants determined from the three lines of lowest J values are a = 49,138.4 mc.; b = 10,603.89 mc.; and c = 9249.20 mc. With the aid of two lines of $C^{13}H_2F_2$ the following structural parameters have been calculated: r_{CF} = 1.358 ± 0.001 Å., r_{CH} = 1.092 ± 0.003 Å., $\angle FCF$ = 108° 17' ± 6', $\angle HCH$ = 111° 52' ± 25'. Stark effect measurements give a dipole moment of 1.96 ± 0.02 debye units.

The structure of methylene fluoride, CH_2F_2, has previously been studied by electron diffraction[3] and by high-resolution infrared spectroscopy,[4] with results in rather poor agreement. The dipole moment has not been reported. The structure of this molecule is of interest in connection with recent radio-frequency and microwave spectroscopic investigations of other halogenated methanes, which have yielded useful information on the nature of the chemical bond.

The available structural information indicated

that CH_2F_2 should be a slightly asymmetric rotor ($\kappa \sim -0.93$) with dipole moment in the axis of intermediate moment of inertia (the C_2 symmetry axis). The magnitude of the reciprocal moments of inertia was such that the only transitions likely to fall below 40,000 mc. would be of the type $\Delta J = +1$, $\Delta K = -1$. (The notation of King, Hainer and Cross[5] will be used, with K understood to mean K_{-1}.) Since transitions of this type are very sensitive to the exact values of the structural parameters, it was impossible to predict with any certainty the transitions which would fall in the accessible frequency region.

A sample of CH_2F_2 was kindly provided by Dr.

(1) The research reported in this paper was made possible by support extended Harvard University by the Office of Naval Research under O.N.R. Contract N5ori-76, Task Order V.

(2) Standard Oil of California Predoctoral Fellow.

(3) L. O. Brockway, J. Phys. Chem., 41, 185 (1937).

(4) H. B. Stewart and H. H. Nielsen, Phys. Rev., 75, 640 (1949).

(5) G. W. King, R. M. Hainer and P. C. Cross, J. Chem. Phys., 11, 27 (1943).

D. E. Kvalnes of the Jackson Laboratory of E. I. du Pont de Nemours and Company. It was reported to contain less than 0.3% impurities; no further purification was attempted. The spectrum was observed on a Stark modulation spectrograph[6] which employed 100 kc. square wave modulation. The measured frequencies should be good to at least 0.10 mc.

Analysis of the Spectrum

An initial search of the region from 17,000 to 31,000 mc. yielded approximately thirty lines of reasonable intensity. Stark effects indicated that most of these lines had fairly high J values. The most prominent feature of the spectrum was the tendency of the strongest lines to occur as close doublets. Since no hyperfine structure should be expected in CH_2F_2, the only reasonable explanation was that these doublets resulted from the asymmetry splitting of levels which would be degenerate in the limiting prolate symmetric rotor. Confirmation of this hypothesis was provided by the intensity variation of the doublets; this agreed well with the 10:6 ratio expected from the nuclear spin weights which result from the equivalent hydrogen and fluorine atoms.

On the basis of partially resolved Stark effects tentative J values could be assigned to three lines. Considering the complexity of the calculations and the large number of transitions which could still be assigned to these lines, a trial and error fit on the basis of this information alone was not practical. Consequently, attention was turned to the doublets in the spectrum. The asymmetry splitting of the J,K level of an almost prolate rotor has been given to first order by Wang[7] in the very convenient form

$$\Delta\nu_{J,K} = [a - \tfrac{1}{2}(b + c)]\, F(J,K)\left(\frac{\beta}{8}\right)^K$$

where

$$F(J,K) = 8\frac{(J + K)!}{(J - K)!(K - 1)!^2}$$

$$\beta = \frac{b - c}{2[a - \tfrac{1}{2}(b + c)]} \qquad a = h/8\pi^2 I_a, \text{ etc.}$$

It is apparent from this formula that the chief contribution to the line splitting will come from the level of smaller K. Rough calculations made by means of Golden's Mathieu function procedure[8] indicated that the doublets above $J = 20$ should tend to fall into series of the type $J, K \rightarrow J + 1, K - 1$; $J + 4, K + 1 \rightarrow J + 5, K$; etc., in which the doublet splitting decreased monotonically with increasing J. The reason for such a grouping, in which J increases by four for each unit increase in K, can be seen from the very approximate equation for the frequency of the transition $J,K \rightarrow J + 1, K - 1$

$$\nu(\text{mc.}) \sim 20,000\,(J + 1) - 40,000\,(2K - 1)$$

With this suggestion as a guide, it was possible to pick out of the observed spectrum a series of six doublets, spaced about 2000 mc. apart, which seemed likely to satisfy the above requirements.

(6) K. B. McAfee, Jr., R. H. Hughes and E. B. Wilson, Jr., *Rev. Sci. Instruments*, **20**, 821 (1949).

(7) S. C. Wang, *Phys. Rev.*, **34**, 243 (1929).

(8) S. Golden, *J. Chem. Phys.*, **16**, 78 (1948).

Application of the Wang splitting formula then confirmed the existence of a true series, as well as providing a value of the asymmetry parameter β. It is seen from the Wang formula that the ratio $\Delta\nu_{J,K}/\Delta\nu_{J+4,K+1}$ is proportional to β. The five experimental splitting ratios formed in this way should therefore be predictable from a single value of β, provided that the J and K values of the beginning doublet are properly assigned. Calculations showed that consistency in this one parameter problem could be obtained only for a small number of assignments. The number was further limited by consideration of the absolute value of the splittings, the intensity alternation of the doublets, the actual intensities of the lines, and finally by using the line frequencies to calculate a set of rough rotational constants. The discovery of another series of doublets at lower frequency was also of help in the analysis. It was possible with this information to make an unambiguous assignment of quantum numbers to each series. The original series ran from $J,K = 20,5 \rightarrow 19,6$ to $J,K = 40,10 \rightarrow 39,11$.

While the identification of the doublet series was the key to the analysis of the spectrum, the large centrifugal distortion at these high J values made it impossible to obtain accurate rotational constants. However, the series did provide a good value of the parameter β, and this knowledge permitted a relatively easy trial-and-error fitting of the lines whose J values had been tentatively identified by Stark effects. A set of rotational constants was thus obtained which explained practically all of the thirty-odd lines observed, while predicting no unobserved lines in the region searched.

The correctness of this analysis was further confirmed by Stark measurements on four lines. The observed Stark effects of the $2_{1,2} \rightarrow 3_{0,3}$, $5_{1,5} \rightarrow 4_{2,2}$, $8_{2,6} \rightarrow 9_{1,9}$, and $9_{2,7} \rightarrow 10_{1,10}$ transitions agreed quite well with the calculated pattern. Since the calculations are sensitive to a large number of perturbing levels, this agreement provides excellent verification for the assignments.

In view of the uncertainty in methods for correcting for centrifugal distortion in general asymmetric rotor transitions, it was decided not to attempt such a correction at the present time. Instead, the frequency range was extended to include the $4_{1,3} \rightarrow 3_{2,2}$ transition at 31,543.75 mc., and this line was used with the $2_{1,2} \rightarrow 3_{0,3}$ and $5_{1,5} \rightarrow 4_{2,2}$ lines to calculate the three rigid-rotor constants. Since centrifugal distortion should be quite low at these J values, it is felt that the constants determined in this way are accurate enough for all present physical applications. (It should be mentioned that an alternative set of rigid-rotor constants, calculated from a least squares fit of six lines of $J < 10$, differed from these by only 0.008%.) The constants obtained from these three lines are given in Table I; this table also includes the approximate rotational constants of $C^{13}H_2F_2$, whose determination is outlined in the next section.

In Table II the observed frequencies of all lines in the spectrum of $C^{12}H_2F_2$ are compared with rigid rotor frequencies calculated from the constants

in Table I. The final calculations were made with continued fractions,[3] and should be accurate to one or two units in the last figure for the transitions of $J < 30$. For the higher J levels, where the convergence was very slow, the computational errors should not exceed 10 mc.

TABLE I
ROTATIONAL CONSTANTS OF CH_2F_2

	$C^{12}H_2F_2$, mc.	$C^{13}H_2F_2$, mc.
a	49,138.4	47,720
b	10,603.89	10,604
c	9,249.20	9,198
$a - (b + c)/2$	39,211.8	37,820
$(b + c)/2$	9,926.54	9,901
κ	−0.932077	−0.9270

TABLE II
OBSERVED AND CALCULATED SPECTRUM OF CH_2F_2

Assignment	Observed frequency, mc.	Calculated frequency	Intensity
$33_{9,24} \rightarrow 34_{8,27}$	17,411.86	18,707	M
$33_{9,25} \rightarrow 34_{8,26}$	17,429.88	18,727	M
$44_{11,34\cdot33} \rightarrow 45_{12,31\cdot32}$	18,972.43	16,674	W
$37_{10,27} \rightarrow 38_{9,30}$	19,034.89	20,816	W
$37_{10,28} \rightarrow 38_{9,29}$	19,039.76	20,822	W
$9_{2,8} \rightarrow 8_{3,5}$	20,237.69	20,226.4	M
$40_{10,30} \rightarrow 39_{11,29}$	20,499.85	18,800	W
$40_{10,31} \rightarrow 39_{11,28}$	20,500.38	18,801	W
$41_{11,30} \rightarrow 42_{10,33}$	20,570.63	22,945	W
$41_{11,31} \rightarrow 42_{10,32}$	20,571.99	22,947	W
?	21,423.20		W
$45_{12,33\cdot34} \rightarrow 46_{11,36\cdot35}$	21,934.33	25,067	W
$8_{2,6} \rightarrow 9_{1,9}$	21,980.68	21,996.1	M
$36_{9,27} \rightarrow 35_{10,26}$	22,135.44	20,922	M
$36_{9,28} \rightarrow 35_{10,25}$	22,137.35	20,924	M
$2_{1,2} \rightarrow 3_{0,3}$	22,204.18	(22,204.18)	M
?	22,579.40		W
$49_{13,36\cdot37} \rightarrow 50_{12,39\cdot38}$	23,188.45	27,198	W
$32_{8,24} \rightarrow 31_{9,23}$	23,864.92	23,030	S
$32_{8,25} \rightarrow 31_{9,22}$	23,871.82	23,038	S
$53_{14,39\cdot40} \rightarrow 54_{13,42\cdot41}$	24,297.52	29,305	W
$14_{4,10} \rightarrow 15_{3,13}$	24,760.40	24,871	S
$28_{7,21} \rightarrow 27_{8,20}$	25,669.29	25,132	S
$28_{7,22} \rightarrow 27_{8,19}$	25,694.13	25,157	S
$24_{6,18} \rightarrow 23_{7,17}$	27,516.98	27,197	S
$24_{6,19} \rightarrow 23_{7,16}$	27,603.66	27,286	S
$5_{1,5} \rightarrow 4_{2,2}$	29,268.90	(29,268.90)	M
$20_{5,15} \rightarrow 19_{6,14}$	29,339.38	29,165	S
$18_{5,13} \rightarrow 19_{4,16}$	29,624.66	29,875	S
$20_{5,16} \rightarrow 19_{6,13}$	29,630.87	29,463	S
$9_{2,7} \rightarrow 10_{1,10}$	30,679.01	30,694.9	M
$16_{4,12} \rightarrow 15_{5,11}$	30,962.08	30,884	S
$4_{1,3} \rightarrow 3_{2,2}$	31,543.75	(31,543.75)	M
$8_{2,6} \rightarrow 7_{3,5}$	31,777.75	31,758	M

The properties of the two series of doublets are presented more clearly in Table III. It is seen that the discrepancy between observed and calculated frequencies, which must be due almost entirely to centrifugal distortion, increases within each series in a roughly exponential manner with increasing K. This variation is smooth enough to permit identification of the unresolved doublets at the end of each series, even though they are shifted by thousands of megacycles from the rigid-rotor frequencies.

Table III also gives a comparison of the observed doublet splittings with those calculated from the Wang formula. The discrepancy here is due partly to centrifugal distortion and partly to the nature of the Wang approximation. Exact calculations by means of continued fractions on the more widely split doublets gave splittings about 4% lower than the Wang formula.

TABLE III
DOUBLET SERIES

J,K^a	$\nu_{obsd.} - \nu_{calcd.}^{\,b}$ mc.	$\Delta\nu_{calcd.}^{\,c}$ mc.	$\Delta\nu_{obsd.}$ mc.	$\Delta\nu_{calcd.}/\Delta\nu_{obsd.}$
19, 6	171	308.70	291.49	1.06
23, 7	319	93.15	86.66	1.07
27, 8	537	27.27	24.84	1.10
31, 9	835	7.81	6.90	1.13
35, 10	1213	2.20	1.91	1.15
39, 11	1700	0.61	0.53	1.15
43, 12	2298	0.17	....	..
33, 9	−1297	20.78	18.02	1.15
37, 10	−1782	5.89	4.87	1.21
41, 11	−2375	1.64	1.36	1.21
45, 12	−3133	0.45	....	..
49, 13	−4010	0.12	....	..
53, 14	−5007	0.03	....	..

[a] For level of smaller J. [b] Taken from Table II. [c] The doublet splitting (including both levels) as calculated from Wang formula.

TABLE IV
STRUCTURAL PARAMETERS OF CH_2F_2

	This research I^a	This research II^b	Infrared[e]	Electron diffraction[d]
r_{CF}, Å.	1.358	1.357	1.32 ± 0.01	$1.36° \pm 0.02$
$\angle FCF$	108° 14'	108° 20'	$107° 0' \pm 30'$	$110° \pm 1°$
r_{CH}, Å.	1.091	1.094	$(1.094)^e$	
$\angle HCH$	112° 6'	111° 38'	$(110°)^e$	

[a] From $2_{1,2} \rightarrow 3_{0,3}$ of $C^{13}H_2F_2$. [b] From $5_{1,5} \rightarrow 4_{2,2}$ of $C^{13}H_2F_2$. [e] Reference 4. [d] Reference 3. [e] Assumed values.

Structural Parameters and Dipole Moment

If the atomic masses[9] are assumed to be known, the three moments of inertia obtained by fitting the spectrum of CH_2F_2 provide three equations in the four parameters which determine the geometrical structure of the rigid molecule. Upon proper choice of coördinate system, these equations can give explicit solutions for two of the parameters; in particular, it can easily be shown that the F–F and H–H distances are given by

$$m_F d^2_{FF} = I_b + I_c - I_a$$

$$m_H d^2_{HH} = I_a + I_b - I_c$$

These relations give $d_{FF} = 2.2005 \pm 0.0001$ Å. and $d_{HH} = 1.8105 \pm 0.0008$ Å. A single equation now relates the two remaining parameters, which may conveniently be taken as the altitudes of the HCH and FCF triangles. In practice it is convenient to assume approximate values for these two quantities and to carry linear correction terms as the two unknowns. A complete solution (in the rigid approximation) now requires one additional relation, which is in principle provided by a single transition of any isotopically substituted species.

If the carbon atom of CH_2F_2 is substituted, the computation is simplified by the following theorem[10]: For any rigid rotor, if an isotopic substitution is made on an atom located on a symmetry axis (and therefore on a principal axis), the new principal moments of inertia are given by (if the symmetry axis is labeled b)

$$I' = I_a + \eta^2 \Delta m(M/M')$$
$$I_b' = I_b$$
$$I' = I_c + \eta^2 \Delta m(M/M')$$

Here primes denote the substituted molecule, M is the total mass, $\Delta m = M' - M$, and η is the distance of the substituted atom from the center of mass of the original molecule. If the original moments are known, the measurement of a single isotopic transition thus permits calculation of the quantity η. In the case of substitution of the carbon atom in CH_2F_2 the equation relating η to the molecular parameters chosen above gives the additional relation that is needed for a complete solution of the structure.

It was possible by searching with a pen and ink recorder to locate in natural abundance the $2_{1,2} \rightarrow 3_{0,3}$ and $5_{1,5} \rightarrow 4_{2,2}$ transitions of $C^{13}H_2F_2$. These lines appeared at 23,501.2 ± 0.4 mc. and 25,829.9 ± 0.4 mc., respectively. Since no other lines of low J values could fall in the region accessible to high-sensitivity searching, it was not possible to make an independent determination of the rotational constants of $C^{13}H_2F_2$. However, each of these lines may be used to calculate a set of structural parameters in accordance with the procedure outlined above; the discrepancy between the two sets then gives an estimate of the validity of the rigid-rotor approximation. The results of this calculation are given in Table IV; the electron diffraction and infrared results are included for comparison. It is seen that the agreement between microwave and electron diffraction parameters is satisfactory, while the infrared C–F distance is out of line. This discrepancy is a consequence of the disagreement in rotational constants. While the infrared value of 39,059 ± 150 mc. for $a - \frac{1}{2}(b + c)$ agrees fairly well with the microwave result, the value 10,671 ± 150 mc. for $\frac{1}{2}(b + c)$ is sufficiently far from our value of 9976.-55 mc. to produce this difference in C–F distance.

The dipole moment of CH_2F_2 was determined from Stark effect measurements on the $M = 1$ component of the $2_{1,2} \rightarrow 3_{0,3}$ transition. The Stark coefficients for this transition were calculated by the method of Golden and Wilson[11]; the direction cosine matrix elements involved were evaluated by a perturbation treatment around the limiting symmetric rotor. Calibrations[12] were carried out by measurements on the OCS line at 24,325.92 mc. The dipole moment obtained in this way is 1.96 ± 0.02 debye units.
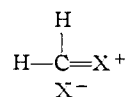
Discussion of Structure

The structural parameters of the simple chlorin-

ated and fluorinated methanes for which microwave data are available are listed in Table V. The most obvious regularity in this series is the shortening of the carbon–halogen distance, in a roughly linear manner, as an additional halogen is added to the molecule. Such a shortening was originally explained by Pauling[13] by the assumption of resonance structures of the type

$$H$$
$$|$$
$$H—C=X^+$$
$$X^-$$

The fact that the C–F shortening is more marked than the C–Cl is attributed to the greater tendency of fluorine to form double bonds. The contribution of structures of this type is also compatible with the increase in the HCH angle as a second halogen is added. However, this simple picture provides no ready explanation of the shortening of the C–H distance, which is especially pronounced in the chlorine case. In this connection it would be interesting to have information on the C–H distance in CHX_3 molecules.

TABLE V

STRUCTURE OF HALOGENATED METHANES

	r_{CX}, Å.	<XCX	r_{CH}, Å.	<HCH	μ, D
CH_3F^a	1.385	.....	1.109	110° 0'	1.81[b]
CH_2F_2	1.358	108° 17'	1.092	111° 52'	1.96
CHF_3^c	1.326			.....	1.59[c]
CH_3Cl^d	1.781	.....	1.113	110° 31'	1.88[e]
$CH_2Cl_2^f$	1.772	111° 47'	1.068	112° 0'	1.62
$CHCl_3^g$	1.761	112° 0'		.....	1.05[h]

[a] O. R. Gilliam, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949). [b] C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **1**, 190 (1933). [c] K. L. Ramaswamy, *Proc. Indian Acad. Sci.*, **2A**, 364 (1935). [d] S. L. Miller, L. C. Aamodt, G. Dousmanis, J. Kraitchman and C. H. Townes, "Structure of the Methyl Halides" (to be published). [e] R. G. Shulman, B. P. Dailey and C. H. Townes, *Phys. Rev.*, **78**, 145 (1950). [f] Reference 14. [g] R. R. Unterberger, R. Trambarulo and W. V. Smith, *J. Chem. Phys.*, **18**, 565 (1950).

While the double-bonding explanation of the variations in this series is qualitatively reasonable, it is by no means unique. The possibility of changes in hybridization has often been suggested to explain such variations in structural parameters. The proposal by Meyers and Gwinn[14] of bent bonds to explain the large Cl–C–Cl angle in CH_2Cl_2 is another approach to the problem. Furthermore, Dr. Richard P. Smith[15] has shown that the shortening of the C–Cl distance can be accounted for on the basis of an inductive effect in the C–Cl bond. Thus there are several distinct approaches which give reasonable qualitative explanations for the observed structural variations, but it is difficult to find arguments to decide which one—or which combination—represents the true physical picture of the chemical bond. It is clear that further experimental data, as well as a more rigorous theoretical approach, will be necessary before the problem is finally solved.

(10) This relation was originally given by Dr. D. K. Coles for linear and symmetric rotor molecules. See "Advances in Electronics," Vol. II, Academic Press, New York, 1950, p. 316.

(11) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

(12) R. G. Shulman and C. H. Townes, *Phys. Rev.*, **77**, 500 (1950).

(13) L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1945, p. 235.

(14) R. J. Meyers and W. D. Gwinn, "The Microwave Spectrum of Methylene Chlorine" (to be published).

(15) R. P. Smith, private communication.

The variation of the dipole moments in Table V deserves special notice. It is seen that the moment of CH_2F_2 is greater than that of CH_3F, in contrast to the trend in the chlorine series. This behavior has been explained by Smith, Ree, Magee and Eyring[16] with their method of calculating charge distributions in halogenated alkanes. In fact,

(16) R. P. Smith, T. Ree, J. L. Magee and H. Eyring, This Journal, 73, 2263 (1951).

their predicted value of 1.91 to 1.93 for the previously unreported CH_2F_2 dipole moment is in good agreement with the present determination.

Thermodynamic Data on the Stannous Chloride Complexes from Electromotive Force Measurements[1]

BY CECIL E. VANDERZEE AND DONALD E. RHODES

The equilibrium constants for the reactions $Sn^{++} + n\ Cl^- \rightleftharpoons SnCl_n^{2-n}$ have been determined by a concentration cell method at two different acidities and four different temperatures, all at a constant ionic strength of 3.0. The hydrolysis constant of stannous ion in the reaction $Sn^{++} + H_2O \rightleftharpoons SnOH^+ + H^+$ has been evaluated from the variation of the cell data with acidity. Heats, free energies and entropies have been determined for the formation of the stannous chloride complexes in the above reactions.

Values of the stability constants of the complex ions formed in stannous chloride solutions were first reported by Prytz,[2] based on e.m.f. data from concentration cells. Recently, Riccoboni[3] and his co-workers studied the same system polarographically and reported values differing considerably from those of Prytz. In both cases correction for the activities of the various ions was made using a form of the Debye–Hückel equation. In neither case was any attempt made to observe the effect of hydrolysis of the stannous ion upon the stannous chloride complexes.

In this paper we present data on the stannous chloride complexes based on concentration cells of the type

Hg(Sn) | Sn(ClO$_4$)$_2$ (x), HClO$_4$ (y), NaClO$_4$ (3-x-y-z), NaCl (z) | Sn(ClO$_4$)$_2$ (x), HClO$_4$ (y), NaClO$_4$ (3-x-y) | (Sn)Hg
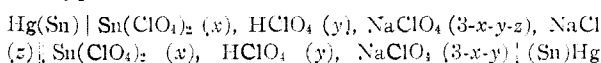
in which x, y and z are concentrations in equivalents per liter, and in which the two-phase tin amalgam is used in the electrodes, following essentially the procedure of Leden[4] in his study of the cadmium complexes. The constant ionic strength of 3 was chosen to permit comparison of our data with the results of Leden[4] and King[5] for cadmium chloride complexes in a sodium perchlorate environment.

Since the mobility of chloride ion is not much different from that of perchlorate ion, we have assumed that a negligible junction potential is formed in the cell as chloride ion is progressively substituted for perchlorate ion up to concentrations of about 0.6 M. Also, with the stannous concentration quite low, about 0.01 M or less, changes in the composition of the cell solution due to complexes should not cause any appreciable junction potential.

We have also assumed, for evaluation of the sta-

bility constants, that the activity coefficients involved will remain essentially constant while chloride ion is substituted for perchlorate ion over the range mentioned. At any constant ionic strength, this assumption is subject to the limitation that the activity coefficients of the species involved depend somewhat upon the specific electrolyte or ions present. The exact nature of this dependence is not known for stannous perchlorate or salts of its type; much of the work on this phenomenon is limited to acids and hydroxides in the presence of simple salts.[6] If one considers stannous perchlorate to be a strong electrolyte of the same type as cadmium nitrate or perchlorate, then its activity coefficients should not vary as greatly with change in ionic strength as those of the strong acids and alkali hydroxides, and probably are not as sensitive to changes in composition of the solution. The activity coefficients of sodium chloride and sodium perchlorate are quite similar,[6] and the two salts exert the same effect upon the activity coefficients of hydrochloric acid in their solutions.[7] These considerations lend some basis for assuming that, for a change in chloride ion from 0 to 0.6 M, the variation of activity coefficients with composition at constant ionic strength will be small for the system we are studying. Until such time as the necessary information regarding the activity coefficients is available, this assumption is necessary in order to obtain information on the stability constants of complex ions; naturally, the limitations of this assumption must be remembered.

Experimental

Materials.—All solutions were prepared with freshly boiled water of conductance grade. To prevent air oxidation of the stannous solutions, all solutions were prepared

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