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, 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.

Acknowledgments.—The author wishes to acknowledge the extensive help of Professor E. Bright Wilson, Jr., in the analysis of this spectrum. Several valuable discussions with Dr. Richard P. Smith are also appreciated.

(16) R. P. Smith, T. Ree, J. L. Magee and H. Eyring, THIS JOURNAL, **73**, 2263 (1951).

[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

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

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The equilibrium constants for the reactions $Sn^{++} + n\ Cl^- \rightleftarrows SnCl_n^{2-n}$ 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 $Sn^{++} + H_2O \rightleftarrows SnOH^+ + H^+$ 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

$$Hg(Sn)\,|\,Sn(ClO_4)_2\ (x),\ HClO_4\ (y),\ NaClO_4\ (3\text{-}x\text{-}y\text{-}z),\ NaCl\ (z)\,\vdots\,Sn(ClO_4)_2\ (x),\ HClO_4\ (y),\ NaClO_4\ (3\text{-}x\text{-}y)\,\vdots\,(Sn)Hg$$

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 stability 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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(1) From the M.S. thesis of Donald E. Rhodes, June, 1951.

(2) M. Prytz, *Z. anorg. allgem. Chem.*, **172**, 147 (1928).

(3) L. Riccoboni, P. Popoff and G. Arich, *Gazz. chim. ital.*, **79**, 547 (1949).

(4) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

(5) E. L. King, THIS JOURNAL, **71**, 319 (1949).

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, chapter 14.

(7) S. R. Bates and J. W. Urmston, THIS JOURNAL, **55**, 4068 (1933).

and stored under nitrogen. For this purpose tank nitrogen was purified for use by the method of Meites and Meites.[8] Reagent grade chemicals were used throughout the work.

Standard stock solutions of sodium perchlorate were prepared by mixing equivalent quantities of sodium carbonate and perchloric acid, using the anhydrous sodium carbonate as a primary standard.

Stock solutions of stannous perchlorate were prepared by the method of Noyes and Toabe.[9] A copper perchlorate solution, prepared by dissolving basic copper carbonate in a twofold excess of 0.5 *N* perchloric acid, was passed through a column packed with granulated tin. The column was kept filled with liquid at all times to exclude air. The resulting stannous perchlorate solution was collected and stored under nitrogen in a storage flask fitted for delivery of the stannous perchlorate solution through a fritted glass filter disk under nitrogen pressure. The solution was analyzed for stannous tin by an iodimetric method. Analysis for free acid content was made by titrating a measured portion of the acidic stannous perchlorate solution with carbonate-free sodium hydroxide to the phenolphthalein end-point, which gave the total equivalents of stannous ion and free acid, according to the work of Prytz.[10] Most of the solutions were about 0.2 *M* in stannous ion and about 0.2 *N* in free acid, and were freshly prepared just before each run or set of runs.

The working solutions were prepared by mixing predetermined quantities of sodium perchlorate, perchloric acid and stannous perchlorate solutions. Solutions containing chloride ion were prepared by adding weighed amounts of sodium chloride. All solutions containing stannous tin were prepared, stored and transferred under nitrogen, and were used immediately after preparation.

Apparatus.—The electrodes were J-shaped lengths of 6-mm. glass tubing, the short arm consisting of a small cup with a short sealed-in platinum wire connecting to a short column of mercury in the long arm for electrical contact. The cup-like portion was filled with molten tin amalgam, prepared by warming thoroughly cleaned metallic tin with triple-distilled mercury. Since the two-phase tin amalgams yield a constant potential,[11] the composition of the amalgam is not critical. Electrodes prepared in this manner were stable and reproducible to 0.03 mv.

The reference half-cell was fitted with a connecting tube ending in a fine fritted glass disk which made the junction with the solution in the working half-cell. Since the reference half-cell was tightly stoppered, once filled, no mechanical flow occurred through the disk.

The working half-cell was a vessel of about 300-ml. capacity whose cap had openings for accessories such as the electrodes, gas delivery tube for nitrogen, a stirrer, buret and thermometer.

During each series of determinations the temperature of the cell was maintained constant to 0.1° or better.

All e.m.f. measurements were made with a Leeds-Northrup type K-2 potentiometer.

Procedure.—After assembling, the cell vessel was thoroughly flushed with purified nitrogen. The reference half-cell was filled with solution under nitrogen, and a carefully measured amount, usually 75 ml., of the same solution was placed in the working half-cell vessel. The cell normally came to equilibrium within an hour, and at equilibrium the potential of the cell seldom differed from zero by more than 0.1 mv.

Measured volumes of solution of the same acidity, stannous content and ionic strength, differing merely in having a known amount of chloride substituted for perchlorate ion, were then added from a buret to the solution in the working half-cell. In calculating the resulting chloride concentration it was assumed that volumes of the solutions were additive. A motor driven stirrer ensured thorough mixing after each addition of solution and hastened attainment of thermal equilibrium. All e.m.f. readings were made with the stirring stopped, and with a slow stream of pure nitrogen passing just over the surface of the solution to keep out oxygen. That this precaution was adequate was shown by tests in which cell potentials remained constant for several hours while the solutions were thus protected.

Results and Discussion

Treatment of Experimental Data.—In an aqueous solution containing stannous and chloride ions there will in general exist the equilibria

$$\mathrm{Sn}^{++} + n\mathrm{Cl}^- \rightleftarrows \mathrm{SnCl}_n^{+2-n} \qquad (1)$$

$$n = 0, 1, 2, 3, 4$$

for which the corresponding equilibrium constants are[12,13]

$$\beta_n = \frac{(\mathrm{SnCl}_n^{+2-n})}{(\mathrm{Sn}^{++})(\mathrm{Cl}^-)^n} \qquad (2)$$

The stannous ion will undergo hydrolysis by the reaction

$$\mathrm{Sn}^{++} + \mathrm{H_2O} \rightleftarrows \mathrm{SnOH}^+ + \mathrm{H}^+ \qquad (3)$$

for which the hydrolysis constant is

$$h = (\mathrm{SnOH}^+)(\mathrm{H}^+)/(\mathrm{Sn}^{++}) \qquad (4)$$

There is, therefore, the possibility of formation of mixed complexes of the general form

$$\mathrm{SnOH}^+ + n\ \mathrm{Cl}^- \rightleftarrows \mathrm{Sn(OH)Cl}_n^{+1-n} \qquad (5)$$

$$n = 0, 1, 2, 3$$

giving the equilibrium constants for the mixed species

$$\delta_n = (\mathrm{Sn(OH)Cl}_n^{+1-n})/(\mathrm{SnOH}^+)(\mathrm{Cl}^-)^n \qquad (6)$$

The concentration of the total stannous tin in the solution will be the sum of the concentrations of the various species containing tin and can be written in terms of the equilibrium constants as

$$(\mathrm{Sn}^{++})_t = (\mathrm{Sn}^{++})\sum_n [\beta_n + \delta_n h/(\mathrm{H}^+)][\mathrm{Cl}^-]^n \qquad (7)$$

where *n* is the number of chlorine atoms per tin atom in the complex.

The e.m.f. of the concentration cell will serve as a measure of the uncomplexed stannous ion, we have then the relation

$$f^0 = \exp(NFE/RT) = 1 + A_1(\mathrm{Cl}^-) + A_2(\mathrm{Cl}^-)^2 + A_3(\mathrm{Cl}^-)^3 + A_4(\mathrm{Cl}^-)^4 \qquad (8)$$

where

$$A_n = \frac{\beta_n + \delta_n h/(\mathrm{H}^+)}{1 + h/(\mathrm{H}^+)} \qquad (9)$$

The above equations require knowledge of the concentration of actual uncomplexed chloride. Letting ν represent the average number of chlorine atoms per tin atom in the complexes, the actual chloride ion concentration is given by

$$(\mathrm{Cl}^-)_a = (\mathrm{Cl}^-)_t - \nu(\mathrm{Sn}^{++})_t\,(f^0 - 1)/f^0 \qquad (10)$$

where ν has any value from 1 to 4, fractions included. It can be shown that

$$\nu = \frac{\mathrm{d}\log(f^0 - 1)}{\mathrm{d}\log(\mathrm{Cl}^-)_a} \qquad (11)$$

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(8) L. Meites and T. Meites, *Anal. Chem.*, **20**, 948 (1948).

(9) A. A. Noyes and K. Toabe, THIS JOURNAL, **39**, 1537 (1917).

(10) M. Prytz, *Z. anorg. allgem. Chem.*, **174**, 355 (1928).

(11) W. J. van Heteren, *Z. anorg. Chem.*, **42**, 153 (1904).

(12) We have assumed that the equilibria are rapid and reversible, particularly the hydrolytic equilibrium. This assumption seemed reasonable, since the cell potentials became constant within a few minutes after mixing each new addition of chloride solution, and would remain constant as long as several hours, as mentioned above.

(13) In the mathematical treatment we have made the necessary assumption, as previously discussed, that the activity coefficients involved will have only a small variation with composition at constant ionic strength. The equations are then treated as if the activity coefficients were constant and equal to unity. Obviously, the values of the constants obtained in this treatment and presented in this paper would take the form $\beta_n = K_n \gamma_{\mathrm{Sn}} \gamma_{\mathrm{Cl}}{}^n / \gamma_{\mathrm{SnCl}n} = K_n/\Gamma_n$, where K_n would be the true equilibrium constant and Γ_n the appropriate activity coefficient factor.

Since only a small fraction of the total chloride present is tied up in the complexes, we can take as a good first approximation in evaluation of ν by equation 11 that $(Cl^-)_a = (Cl^-)_t$. In fact, the approximation that $d \log(Cl^-)_a = d \log(Cl^-)_t$ is even better. Actually, quite satisfactory values of ν were obtained from the measured slopes of a plot of $\log (f^0 - 1)$ against $\log (Cl^-)_t$. Slightly better values of ν could be obtained by a second approximation, either by plotting $\log(f^0 - 1)$ against the first approximation to $(Cl^-)_a$ and repeating the determination of ν, or more simply by determining the quantity $d \log(Cl^-)_t/d \log(Cl^-)_a$ from the first approximation to $(Cl^-)_a$ and correcting the first approximation to ν by this factor, which is in practice nearly constant and for these runs is very near 0.98. The magnitude of this correction is not much greater than the inherent error in determining ν from the slopes of the curves. The difference between the first and second approximations for these data is of the order of 1 to 2 parts per 1000 in $(Cl^-)_a$, rapidly becoming less as the chloride concentration increases.

Several methods are available for evaluation of the constants in equation 8. In most of this work the method of Leden[4] was applied, since it permits the advantage of judicious graphical smoothing of the data, and yielded values in good agreement with those obtained by a least squares method.

Values of the Constants A_n.—Values of A_1, A_2 and A_3 were determined for 0.1 and 0.5 N acid at 0, 25, 35 and 45° and are shown in Table I. For the runs at 45° the value of A_4 lay between 10 and 20; for most of the other runs all that could be established was that A_4 was somewhere between 0 and 10. These low values of A_4 indicate that within the range of data obtained, no significant amount of $SnCl_4^=$ was present.

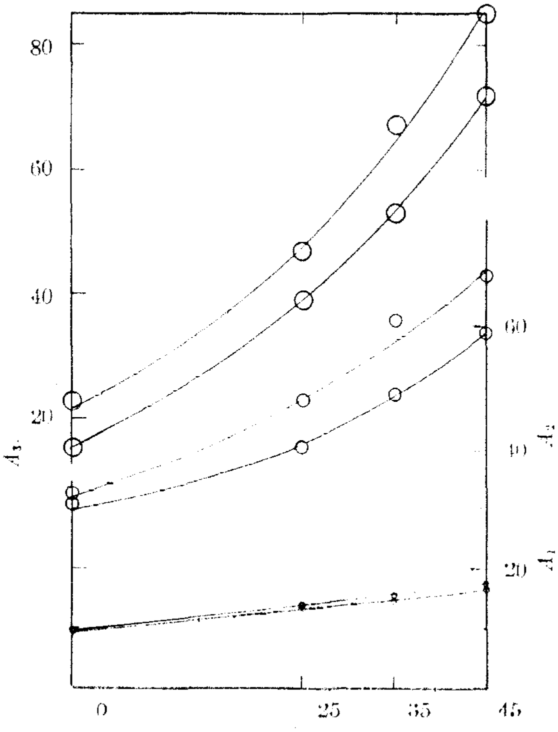

Fig. 1.—Variation of constants with acidity and temperature. Upper curve in each set is for 0.5 N acid, lower curve for 0.1 N.

An estimate of the precision of the method is obtained by comparison of the constants obtained from the several runs in 0.5 N acid at 25°. The average deviations of the constants from their mean values are shown in Table I.

TABLE I[a]

OBSERVED VALUES OF THE CONSTANTS A_n

Temp., °C.	Acidity, eq./liter	A_1	A_2	A_3
0.0	0.1000	9.05	30.9	15
0.0	.5000	9.20	32.5	23
25.0	.1000	13.6	40.4	39
25.0[b]	.5000	13.8 ± 0.1	48.0 ± 1	47 ± 5
35.0	.1000	14.4	49	53
35.0	.5000	16.0	61.5	67.5
45.0	.1000	16.5	59	72
45.0	.5000	18.0	68	85

[a] All concentration units in moles per liter. [b] Mean of seven runs.

TABLE II

SUMMARY OF EXPERIMENTAL DATA[a]

$(Cl^-)_t$ (eq./l.)	E.m.f., millivolts							
	Total Sn^{++} 0.0103 M				Total Sn^{++} 0.0099 M			
	Acidity 0.5000 M				Acidity 0.1000 M			
	0°	25°	35°	45°	0°	25°	35°	45°
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
.01	0.98	1.50	1.80	2.00	0.96	1.41	1.57	1.78
.02	1.90	2.94	3.46	3.90	1.88	2.78	3.10	3.51
.03	2.83	4.35	5.07	5.75	2.80	4.12	4.56	5.20
.05	4.64	7.03	8.15	9.11	4.60	6.72	7.35	8.42
.07	6.40	9.45	10.90	12.15	6.35	9.10	9.95	11.40
.10	8.90	12.80	14.70	16.25	8.82	12.30	13.45	15.42
.15	12.84	17.75	20.20	22.15	12.65	17.10	18.70	21.25
.2	16.35	22.10	25.05	27.35	16.00	21.30	23.40	26.25
.3	22.4	29.6	33.0	36.1	21.8	28.3	31.0	34.4
.4	27.5	35.7	39.6	43.1	26.8	34.3	37.3	41.3
.5	32.0	40.9	45.2	49.0	31.3	39.3	42.7	47.0
.6	36.1	45.5	49.9	55.0	35.6	43.7	47.3	52.0

[a] Taken from large scale graphs of e.m.f. against $(Cl^-)_t$ for rounded values of Cl^-_t. The values tabulated here represent the original data to 2 parts per 1000; the reproducibility of the data, as shown by several runs at 25° and 0.5 M acidity, was of the order of 5 parts per 1000.

The Hydrolysis Constant of Stannous Ion.—To better illustrate the variation of the constants A_n with acidity and temperature, the data in Table I are presented graphically in Fig. 1. The very small variation of A_1 with acid concentration is in sharp contrast with the larger and almost equal variations in A_2 and A_3. From the nature of the function defining A_n it is seen that if δ_n and β_n are equal, A_n will not vary with acidity; if δ_n is less than β_n, then A_n will increase with increasing acidity, while if δ_n is greater than β_n, then A_n will decrease with increasing acidity. The small variation in A_1 suggests that δ_1 is only *slightly less* than β_1, while the larger variation in A_2 and A_3 suggests that δ_2 and δ_3 are *much less* than β_2 and β_3, respectively. The nearly equal fractional variation in A_2 and A_3 suggests a nearly common small value for δ_2 and δ_3. The tendency to form negatively charged mixed complexes of the type defined by δ_2 and δ_3 may reasonably be expected to be less than the tendency to form the species $Sn(OH)Cl$, again suggesting very small values of δ_2 and δ_3 in comparison with

β_2 and β_3. From these considerations it seemed reasonable to take

$$A_2 = \frac{\beta_2}{1 + h/(\mathrm{H}^+)} \text{ and } A_3 = \frac{\beta_3}{1 + h/(\mathrm{H}^+)}.$$

Using these relations and the observed variations of A_2 and A_3 with acidity, the hydrolysis constant h was found to have the values 0.016, 0.020, 0.024 and 0.025 at 0, 25, 35 and 45°, respectively. Values of h obtained from A_2 were in consistent agreement with those obtained from A_3 values. The above values for the hydrolysis constant are in satisfactory agreement with values reported by Garrett and Heiks[14] (0.0085, ionic strength = 0) and Gorman[15] (0.02, ionic strength = 0) at 25°.

Values of the Several Stability Constants.—Using the above values for the hydrolysis constant it is then possible to determine δ_1 as well as the constants β_1, β_2 and β_3. A summary of the several computed constants is given in Table III.

TABLE III

SUMMARY OF COMPUTED EQUILIBRIUM CONSTANTS

	0°	25°	35°	45°
h	0.016	0.020	0.024	0.025
δ_1	8	11	7	12
β_1	9.25	14.0	16.5	18.5
β_2	34	50	60	72
β_3	23	48	68	90

While this work was in progress Duke and Courtenay[16] reported values at 25° for the constants β_1, β_2, β_3 and β_4 in perchloric acid media, ionic strength 2.03, as 11.3 ± 0.2, 57.5 ± 3, 13.8 ± 4 and 13.8 ± 11, respectively. They also used a potentiometric method, but evaluated the constants by first determining β_1 from the limiting slope of f^0 against (Cl$^-$) as (Cl$^-$) becomes zero, then using this value of β_1 and three points on the curve to set up a third order determinant which was solved for the other three constants. We have re-examined the data in their paper and believe it can be satisfactorily represented by the three constants $\beta_1 = 11.6$, $\beta_2 = 52$ and $\beta_3 = 33$ with about the same limits of precision as they have reported. In any case, considering the difference in ionic strength and acidity, the agreement with their results seems to be satisfactory.

We could find little evidence to support a value of β_4 greater than about 10 except possibly at 45°. At the other temperatures, three constants describe the data within experimental accuracy. Attempts to fit the data with a slightly smaller value of β_3 and a finite small value of β_4, about 5, gave no better representation of the data. We can only conclude that β_4 must be somewhat smaller than 10 and cannot be established more precisely from these data.

Some consideration of the accuracy and significance of the values reported for the constants is necessary. The estimation of the actual chloride concentration has been discussed; since the correction for complexed chloride is small, changes in activity coefficients with composition very probably do not introduce uncertainty there. The method used to evaluate the constants A_1, A_2 and A_3 allows one to establish these values with considerable confidence. In Table I are shown the average deviations from the mean for several runs. While the precision with which the constants can be evaluated for any particular run is slightly better than these deviations from the mean, we feel that the probable errors in the constants A_1, A_2 and A_3 are about 1.5, 4 and 8%, respectively. Consequently the values of δ_1 and h which are obtained from them may be uncertain to 20 or 30%. These uncertainties do not appreciably affect the calculation of β_1, β_2 and β_3, since the ratio h/H^+ is small in any case. As pointed out by one of the Referees, the substitution of hydrogen ion for sodium ion may influence the activity coefficient factors to some extent. While the magnitude of this effect is unknown, it will probably not be the major influence since the ratio h/H^+ is quite small. We estimate the probable errors in β_1, β_2 and β_3 to be about 2, 5 and 10%, respectively.

TABLE IV

FREE ENERGY, HEAT CONTENT AND ENTROPY CHANGES AT 25° FOR THE REACTIONS: $\mathrm{Sn}^{++} + n\mathrm{Cl}^- \rightleftarrows \mathrm{SnCl}_n^{+2-n}$

Complex formed	ΔF, cal./mole	ΔH, cal./mole	ΔS, cal./deg./mole
SnCl^+	−1570 ± 15	2600 ± 400	14.0 ± 1.4
SnCl_2	−2330 ± 30	3200 ± 800	18.5 ± 2.6
SnCl_3^-	−2310 ± 60	5600 ± 1500	26.5 ± 5.2

Heats and Entropies of Some of the Complexes.—The changes in heat content, free energy and entropy for the formation of several of the complexes were computed from the data in the usual manner, and are summarized in Table IV. These quantities will be those for the reactions occurring in a medium of ionic strength 3.0 (with sodium perchlorate as the inert salt) rather than for the systems in their usual standard states, but allow useful comparison with other data in the literature obtained for similar conditions.

Comparison with the results of King[5] for the cadmium chloride complexes shows both sets of values to be of the same general magnitude. The highly endothermic process for formation of SnCl_3^- parallels that for CdCl_3^-. On the other hand, the SnCl_2 complex is formed endothermally while King found the CdCl_2 complex to be formed exothermally. Whether or not this is due to individual differences between the species is not certain. In both cases, if one assumes that the trend in heats and entropies of formation is continued for the tetrachloro species, then the fraction present as that species must be relatively small except at high chloride concentrations or at high temperatures.

LINCOLN, NEBRASKA

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[14] A. B. Garrett and R. E. Heiks, THIS JOURNAL, **63**, 562 (1941).

[15] M. Gorman, *ibid.*, **61**, 3342 (1939).

[16] F. R. Duke and W. G. Courtenay, *Iowa State Journal of Science*, **24**, 397 (1950).