

The transference numbers are given by

$$t_{\text{Cd}^{++}} = 0.370 + 4.08E \quad \text{above } m(\text{ref})$$

$$t_{\text{Cd}^{++}} = 0.384 \quad \text{below } m(\text{ref})$$

Values for the experimental concentrations are given in Table II.

Discussion

Purser and Stokes³ point out that zinc amalgams deteriorate unless protected from oxygen. Apparently, the measurements of Wolten and King were inaccurate because the solutions were not deaerated and protected. Triplicate cells agreed well since the amalgam was prepared in small lots and was uniform for each set of cells.

Some of the transference numbers found for cadmium ion are plotted *vs.* \sqrt{m} in Fig. 1, with values found by the Hittorf method at 18°, as

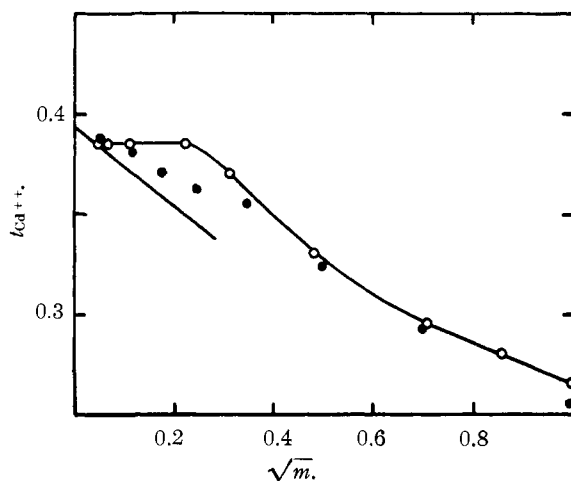


Fig. 1.—Transference numbers in cadmium sulfate: O, this work, 25°; ●, values summarized by Jahn, 18°; slope of straight line, -0.193 .

summarized by Jahn.¹⁰ The temperature difference would affect only the third decimal place.

No data have been found from which the limiting conductance Λ^0 for cadmium sulfate at 25° may be established. At 18°, $\Lambda^0_{\text{CdSO}_4}$ is about one unit lower¹¹ than $\Lambda^0_{\text{ZnSO}_4}$, and if the temperature coefficients are the same, $\Lambda^0_{\text{CdSO}_4}$ may be taken as 132. Since $\lambda^0_{\text{SO}_4^{--}} = 80$, the limiting transference number $t^0_{\text{Cd}^{++}}$ should be 0.393 and the limiting slope *vs.* \sqrt{m} should be¹² -0.193 . These values are indicated by the straight line of Fig. 1. Corresponding values for zinc ion are³ 0.398 and -0.184 .

It is believed that values of E in the tables are correct to better than 0.5 mv., with the possible exception of one or two points nearest $m(\text{ref})$ in each case. In obtaining the relation between E_t and E , it may be better to use a graphical rather than a least squares method, or in some way give points near $m(\text{ref})$ least weight. The graphical method was used in the case of cadmium sulfate.

Consistency of the data may be shown by plotting E_t *vs.* E below $m(\text{ref})$, E_t/E *vs.* E above $m(\text{ref})$. If E contained irregular errors, the points would not lie near a smooth line. If all errors in E were in the least favorable direction, which is unlikely, t_+ could differ as much as 0.01 at $m(\text{ref})$ and 0.005 or less at other concentrations. It seems more probable that no value of t_+ is in error by more than 0.005. It is, of course, quite certain that t_+ does not become negative at any concentration employed.

Errors of interpolation of the e.m.f. of cells without transference, and use of activity coefficients, could be avoided by including zinc and cadmium electrodes in the cells to measure E directly at each concentration.

(10) H. Jahn, *Z. physik. Chem.*, **58**, 641 (1907).

(11) "Landolt-Börnstein Tabellen," 5th Edition, Vol. II, p. 1080.

(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 1st Edition, Reinhold Publ. Corp., New York, N. Y., 1943, pp. 172, 537.

NEW YORK 3, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF KANSAS]

Mechanism of the Tungstate Catalyzed Reduction of Perchlorate by Stannous Chloride

BY G. P. HAIGHT, JR.¹

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The reduction of perchlorate by stannous chloride is catalyzed by the presence of tungstate in concentrated hydrochloric acid. The reaction is zero order with respect to stannous and first order with respect to perchlorate and tungstate. Catalysis is attributed to complex formation between tungstate and perchlorate. This reaction is discussed in terms of information on the catalytic reduction of perchlorate by stannous tin using both tungstate and molybdate as catalyst.

Introduction

The catalytic effect of tungstate on the reduction of perchlorate observed polarographically by Laitinen and Ziegler² has been found to be maintained when stannous chloride is substituted for the dropping mercury electrode. This is especially interesting in view of the previously observed catalytic

effect of molybdate on the reduction of perchlorate polarographically,^{3,4} with stannous ion,⁴ and with metallic zinc.^{5a,b} To study the tungstate catalysis high concentrations of HCl must be used to prevent precipitation of tungstic acid. Under these conditions molybdate does not catalyze the reduction by stannous chloride since molybdenum is reduced to the trivalent form which is inert.⁴ Laitinen and

(1) Department of Chemistry, Swarthmore College, Swarthmore, Penna. Paper presented at the 126th Meeting of the A.C.S., New York, N. Y., September, 1954.

(2) H. A. Laitinen and W. A. Ziegler, *THIS JOURNAL*, **75**, 3045 (1953).

(3) R. Holtje and R. Geyer, *Z. anorg. Chem.*, **246**, 265 (1941).

(4) G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

(5) (a) G. P. Haight, Jr., and W. F. Sager, *THIS JOURNAL*, **74**, 6056 (1952); (b) G. P. Haight, Jr., *Anal. Chem.*, **25**, 642 (1953).

Ziegler² attributed the tungstate catalysis to the reduction of tungsten to the pentavalent state which is rapidly oxidized by perchlorate. The reduction takes place at potentials more positive than that for the anodic dissolution of mercury so that only the total current resulting from the process is observed and not the actual polarographic wave. The assumption, however, is not unreasonable in view of the fact that tungsten is reduced to the pentavalent state under such conditions and that reduction to the trivalent form at more negative potentials appears to decrease the catalysis. A study of the kinetics of reduction with stannous chloride seems to rule out pentavalent tungsten as an intermediate in that case. In 10 to 11 *M* hydrochloric acid, 0.01 to 0.25 *M* SnCl₂ and HClO₄, and 10⁻³ to 10⁻² *M* tungstate, the kinetics follow a scheme described by $d(\text{Sn}^{++})/dt = K(\text{W}^{\text{VI}})(\text{ClO}_4^-) + K'$. Chloride in addition to preventing polytungstate formation apparently hinders tungstate-perchlorate interaction. Evidence is given for not considering lower valences of tungsten as participants in the reaction. The possibility of complex formation between tungstate and perchlorate is considered and a comparison made between mechanisms of molybdate and tungstate catalyses.

Experimental

All reagents were of analytical grade and were used without further purification. A stock solution of stannous chloride was prepared by dissolving 0.25 mole in 250 ml. of concd. HCl in a narrow-neck glass-stoppered flask. Laitinen and Ziegler reported that oxygen did not interfere with polarograms in concentrated hydrochloric acid due to the high vapor pressure of hydrogen chloride gas. However, the stannous ion stock solution concentration decreased 20% in three weeks and blank losses on runs were observed which were nearly independent of perchlorate concentration. This loss of reducing power is attributed to oxygen from the air getting to solutions during removal of samples for titration. Perchloric acid which was standardized with sodium carbonate was used as a source of perchlorate ion. 0.1 molar sodium tungstate was dissolved in water after weighing the dihydrate. No standardization was deemed necessary. This solution was diluted to 0.033 and to 0.01 *M*. Runs were made up by adding 40 ml. of concd. hydrochloric acid to 5 ml. of a tungstate solution and about 1 ml. of perchloric acid solution depending on the concentration of perchlorate desired. The reaction was started by adding 5 ml. of stannous chloride stock solution. Attempts to start the reaction by adding aqueous tungstate last proved ineffectual since great quantities of tungsten blue formed and an induction period of several hours preceded reduction of perchlorate. With the tungsten already in the strong acid solution addition of stannous chloride caused only a pale blue color to appear and the reduction of perchlorate began at once.

Five-ml. samples of the reaction mixture were quenched in 100 ml. of water and titrated with 0.025 *N* potassium permanganate. The chloride present caused slow fading of the end-point but did not interfere with the titration of stannous ions. The reaction was thermostated at 35° which enabled runs to be made over convenient periods ranging from one hour to three days. Stannous chloride is known to reduce perchloric acid in concentrated hydrochloric acid at temperatures upwards of 60°. Blank runs with no tungstate were roughly 30% faster when perchloric acid was present in 10-fold excess than when present in concentration equivalent to stannous present. Perhaps there was a slight contribution to the blank by direct reduction of perchlorate but this was not of particular significance except to alter the blank correction slightly in runs of high perchlorate. The results of several runs are shown in Table I. *K'* values were evaluated from blank runs. *K* values were calculated according to the equation

$$\frac{-d(\text{Sn}^{++})}{dt} = K(\text{W}^{\text{VI}})(\text{ClO}_4^-) + K' \quad (1)$$

This on integration yields

$$-(\text{Sn}^{++}) = (K(\text{W}^{\text{VI}}\text{ClO}_4) + K')t + C \quad (2)$$

In the equivalent case where *K'* can be ignored

$$\ln(\text{Sn}^{++}) = \frac{K(\text{W}^{\text{VI}})}{4} + C \quad (3)$$

If

$$(\text{ClO}_4^-) = \frac{A + (\text{Sn}^{++})}{4} \text{ where } A = 4(\text{ClO}_4^-)_0 - (\text{Sn}^{++})_0$$

$$\frac{-d(\text{Sn}^{++})}{dt} = \frac{K(\text{W}^{\text{VI}})}{4} [A + K't + (\text{Sn}^{++})] + K' \quad (4)$$

An attempt was made to determine the chloride dependence of the reaction by increasing perchloric acid concentration from 10- to 50-fold at the expense of hydrochloric acid maintaining what might be called "constant ion strength" though this term has little significance in 10 *M* acid. This necessitated cutting the tungstate concentration down to allow for increased rate of reaction. Apparently the rate is inversely proportional to the square of the chloride activity. Results are difficult to analyze for the high HClO₄ concentration increased the activity of HCl so much that it boiled out vigorously with perceptible cooling of the reaction flask. The results obtained are given in Table II. This study was made at 25°. Activities were estimated by extrapolating the data of Akerlof and Teare⁶ for hydrochloric acid and those of Rosenfeld⁷ for perchloric acid to the total molality (HCl + HClO₄) of each solution and then using Guggenheim's theory of interaction⁸ to obtain individual activity coefficients for HCl and HClO₄ in each mixture.

Since the estimated activities used are mean ionic activities, not those for chloride and perchlorate ions themselves, and since the activity of tungstate is indeterminate, the *K'* values can be regarded as only gross approximations, but the agreement is notable and suggests that a complex of two chloride ions with a tungstate ion inhibits the catalysis. The higher values of the last four runs may be accounted for by the fact that some hydrogen chloride boiled out of each of these solutions, making their chloride concentrations actually less than those used in the calculations. This would lead to higher calculated *K''* values than true since *K''* is proportional to the square of the activity of hydrochloric acid. The value of *K''* was calculated as well from the polarographic data of Laitinen and Ziegler² and a value of 25,000 mole/l./hr. was found for solutions 0.3 *M* in HCl and 11.5 *M* in HClO₄. At lower HCl concentrations deviations to much higher values were noted indicating a break down of chloride inhibition.

Discussion

In runs of high perchlorate concentration *K* was evaluated from the slope of the straight line plot for (Sn⁺⁺) vs. *t* as shown in Fig. 1. The slope was corrected for *K'* as determined from a blank run. For two runs in which (Sn⁺⁺) was equivalent to (ClO₄⁻), *K'* was not a large factor and by ignoring it, *K* may be evaluated from the slope of -log (Sn⁺⁺) vs. *t* as shown also in Fig. 1. For one run the deviation from a straight line for the log (Sn⁺⁺) vs. *t* plot was very great since the catalyzed reaction had approximately the same speed as the blank. In this case *K* had to be evaluated from the initial slope of (Sn⁺⁺) vs. *t* which is not too certain a quantity for this system in view of the induction period observed when tungsten blue is produced in large quantities.

The fact that the reaction is first order in perchlorate and tungstate, respectively, and zero order

(6) G. Akerlof and J. W. Teare, *THIS JOURNAL*, **59**, 1855 (1937).

(7) Landolt-Bornstein, "Physikalische-Chemische Tabellen," Eng. B. III, 2144 (1936).

(8) E. A. Guggenheim, *Phil. Mag.*, [7] **19**, 588 (1935).

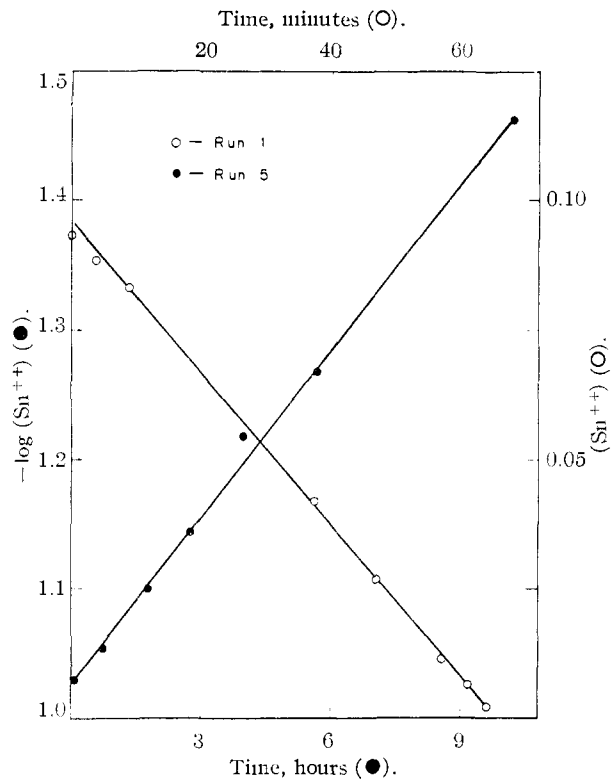
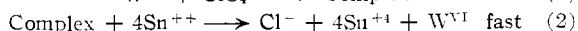
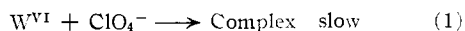


Fig. 1.

in stannous tin suggests a slow step involving interaction of tungstate with perchlorate and a fast step involving stannous tin. A mechanism consistent with that of Laitinen and Ziegler would involve rapid reduction of tungstate by stannous followed by slow reoxidation of reduced tungsten by perchlorate. In the concentration of hydrochloric acid used, stannous ion reacts very slowly with hexavalent tungsten giving a pale blue solution with maximum color intensity appearing only after several hours. An attempt to titrate hexavalent tungstate in concd. hydrochloric acid with stannous chloride potentiometrically indicated virtually no reaction. A few drops of stannous chloride solution gave the stannous potential despite the presence of a large excess of tungstate. The possibility of interaction of perchloric and hydrochloric acids in the presence of tungstate to give chlorine which would rapidly oxidize stannous chloride was tested by allowing a run to stand for several hours before adding stannous chloride. No appreciable build up of oxidizing power was observed. Substitution of ferrous for stannous indicated other reducing agents may be used but different rates of reaction are obtained. The oxidation of ferrous was very much slower and appeared not to be catalyzed by tungstate. It seems apparent that hexavalent tungsten is the catalyst and it is proposed that it acts by forming a complex which is rapidly reduced to give hexavalent tungsten and chloride by the equations



Reaction 2 must be fast enough to prevent the establishment of equilibrium in reaction 1. This

corresponds to an assumption made regarding the catalysis by Mo^{IV} of the reduction of lower oxidation states of chlorine by stannous ion in a previous study.⁵ It was found necessary to propose complex formation between perchlorate and both Mo^{VI} and Mo^{IV} in the previous study. Tungsten seems both better able to form complexes and better able to remain bound to oxygen than does molybdenum. Previously Haight and Sager⁵ have suggested that these reactions may proceed by transfer of oxygen atoms. If this is the case stannous tin apparently removes oxygen bound to molybdenum in the complex $[\text{Mo}^{\text{VI}}\text{ClO}_4^-]$ and from the perchlorate in the complexes $[\text{W}^{\text{VI}}\text{ClO}_4^-]$ and $[\text{Mo}^{\text{IV}}\text{ClO}_4^-]$. It is noted here that hexavalent tungsten is more easily reduced (to tungsten blue) when it is complexed with itself, that is, reduction by stannous ion is virtually eliminated in concentrated hydrochloric acid apparently because this acid prevents polytungstate formation. Thus hydrochloric acid aids the catalysis by hindering tungstate polymerization and at the same time hinders the catalysis by preventing complex formation between hexavalent tungsten and perchlorate. Recently Duke and Quinney⁹ have proposed that titanous ion is effective in reducing perchlorate because of complex formation. Apparently oxyphilic transition metal ions may form very weak complexes with perchlorate and render it susceptible to attack by reducing agents. Laitinen and Ziegler observed that hydrochloric acid suppressed the catalytic reduction of perchlorate polarographically and that it also suppressed the direct interaction of mercury with tungsten.

TABLE I

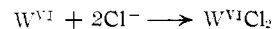
RESULTS OF RUNS IN 10 MOLAR HCl

$(\text{Sn}^{++})_0$, mole/l.	$(\text{ClO}_4^-)_0$, mole/l.	(W^{VI}) , moles/l.	K' , moles/l./hr.	K , 1./mole/hr.	T , °C.	
0.0933	0.0233	10^{-2}	6×10^{-4}	42.8 ^a	40.0 ^b	35.5
.0933	.0233	3.33×10^{-3}	6×10^{-4}	39.6 ^a	41.2 ^b	35.5
.0933	.0233	10^{-3}	6×10^{-4}	34.5 ^a		35.5
.0933	.227	10^{-3}	7.9×10^{-4}	39.5 ^c		35.5
.0933	.227	3.33×10^{-3}	7.9×10^{-4}	46.0 ^c		35.5
.0913	.0518	10^{-2}	6×10^{-4}	36.9 ^a	39.1 ^b	35.5
.073	.0454	3.33×10^{-3}	6×10^{-4}	43.0 ^a	35.9 ^b	35.5
.0735	.227	10^{-3}	7.9×10^{-4}	35.9 ^c		35.5
.10	.227	10^{-2}	20.00 ^d		25.0
.091	.227	10^{-2}	0.92 ^d		0.0
.104	.227	10^{-2}	1.01 ^e		0.0

^a From initial slope of (Sn^{++}) vs. t and equation 4.

^b From $\log (\text{Sn}^{++})$ vs. t ignoring effect of K' . ^c From $d(\text{Sn}^{++})/dt = K(\text{W}^{\text{VI}})(\text{ClO}_4^-) + K'$ taking average value of $[\text{ClO}_4^-]$ as constant during run. ^d Solution very blue at first. ^e Solution only pale blue.

The data shown in Table II may be explained by the formation of a complex of tungstate with two chloride ions which, by competing with perchlorate



ions for sites on tungstate, inhibit the catalysis. The analysis of the data in this case, however, involves too much conjecture to say anything more definite than that a complex is formed between tungstate and chloride which inhibits complex formation between tungstate and perchlorate.

(9) F. P. Duke and Paul Quinney, Paper at 125th Meeting of A. C. S., Division of Analytical Chemistry.

TABLE II
EFFECT OF VARYING HCl
 K' ignored, $T = 25^\circ$

(Sn ⁺⁺) ₀ , moles/l.	(ClO ₄ ⁻) ₀ , moles/l.	(WV ¹) ₀ , moles/l.	(HCl) ₀ , moles/l.	K_1 , l./mole/ hr.	$K^{1/b}$, moles/l./ sec.
0.1	0.227	10 ⁻²	10.00	20.0	36,000
.1	2.27	10 ⁻³	7.77	31.8	53,000
.1	4.54	4 × 10 ⁻⁴	5.56	51.4	65,300
.1	6.81	2 × 10 ⁻⁴	3.33	110.0	59,300
.06 ^a	7.94	2 × 10 ⁻⁵	2.25	257.0	65,000

^a As SnSO₄. ^b K'' calculated from $-d(\text{Sn}^{++})/dt = K''(WV^1)^{a_{\text{HClO}_4}}/a_{\text{HCl}}$.

There is indication that two chlorides are involved. There is also a suggestion that the polarographic

reduction and stannous chloride reduction proceed by the same mechanism.

The variation of K with temperature does not follow well the usual proportionality between $\log K$ and reciprocal T . However, the energy of activation seems to lie between 12000 and 17000 cal. comparing very well with the activation energy found by Laitinen and Ziegler for the polarographic reduction.

The author wishes to express thanks for the interest and helpful suggestions received from Professors W. J. Argersinger and A. W. Davidson. This work was sponsored by the Office of Ordnance Research, U. S. Army.

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[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, PLASTICS DIVISION RESEARCH DEPARTMENT]

Solid-Liquid Equilibria of the System NaCN-NaOH-H₂O¹

BY GEORGE D. OLIVER AND S. E. J. JOHNSEN

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Ternary phase diagrams, expressed in weight %, were determined for three isotherms, 25, 35 and 55°, on the system NaCN-NaOH-H₂O. There were two isothermally invariant points, hydrates and anhydrous salts found on each isotherm. A new double compound, NaCN·NaOH, of equimolar composition found at 35 and 55°, did not exist at 25°. A NaOH concentration greater than 10% prevented the formation of NaCN·2H₂O at 25°. Density values were determined on some samples at each temperature.

Introduction

In the course of fundamental research on cyanide solutions, interest developed in the behavior of NaCN and NaOH in a ternary system with water. The small amount of data in the literature were not sufficient to establish the desired phase relationships; therefore, the ternary phase diagrams were determined at 25, 35 and 55°. These isotherms were chosen for the following reasons. At 25° both solid components are precipitated as hydrates from binary solutions. At 35° anhydrous NaCN is precipitated, but at 34.7° the dihydrate is the stable form. The solubility of each salt in water is approximately 50 weight % at 55°.

Experimental

Materials.—Both compounds were J. T. Baker reagent grade material. Assays showed a purity of 97.2% for NaCN and 97.7% for the NaOH. No attempt was made to purify either compound; however the carbonate formed in the strong NaOH solutions was removed by filtration.

Procedure.—A series of 100-g. samples were prepared by weighing, to the nearest 0.1 g., the required amount of NaCN, NaOH and H₂O into a flask. After heating to promote solution, the samples were filtered to remove the carbonate and transferred to 200-ml. glass tubes.

Equilibrium was attained in the samples by agitating for 4 to 5 hours in a thermostated bath ($\pm 0.05^\circ$) by means of a rocking mechanism. An analysis of duplicate samples that had been agitated for 2 and 24 hr. proved that a short agitation time was sufficient for equilibrium. Usually, the samples were allowed to stand in the bath overnight so that the solid phase could settle out. After sampling the liquid with a pipet, it was either decanted from the tube or removed by suction through a glass filter stick so that the solid phase could be sampled. The filter stick was necessary in most cases on the samples of high NaOH content since the solid phase did not settle compactly.

A satisfactory method of analyzing a solution for both cyanide and base was not found in the literature. Therefore, the analytical procedure for determining the composition of the solubility samples was established by carefully preparing four samples that varied from 5 to 45% of each compound. These samples were titrated first with 0.1 *N* AgNO₃ (Liebig's method) to determine the cyanide content; then the same aliquot was titrated with 0.1 *N* H₂SO₄, to determine the NaOH content. Phenol red was the indicator employed. It was found necessary to remove the cyanide ion from solution before analyzing for the base since HCN is formed and liberated in acid solution. The accuracy of the analytical procedure was very satisfactory, although in highly concentrated NaOH samples more dilution was required to give a satisfactory end-point for the cyanide analysis.

In the analysis of the solubility samples two to three-gram aliquots were taken from the liquid and from the wet solid. After diluting to 250-ml. volume, an aliquot of 25 or 50 ml., depending on the basicity, was used for the titration. Accordingly, the results were expressed in weight percentage. Schreinemaker's "Method of Wet Residues"² was used to determine the composition of the "dry salt." This method enables one to analyze the solid phase wet with the mother liquor.

Density values were determined on the mother liquor of several samples at each temperature. At 25 and 35°, they were determined with a simple Westphal balance to four significant figures. At 55°, a 10-ml. pipet was heated to 55° and filled with the supernatant liquid; then the tube was cooled to room temperature where the sample either solidified or became too viscous to flow from the pipet. The difference in the weights of the full and empty pipet, divided by ten, was the density in g./ml. Density values were not determined on samples of high NaOH content because of their viscosity.

Results and Discussion

A summary of the solubility data and density values are given for 25, 35 and 55° in Table I. These isotherms are plotted on trilinear diagrams,

(1) Presented at the American Chemical Society Meeting, Chicago, Illinois, September, 1953.

(2) J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 323.