ing such a solution with an equiconcentrated but nearly neutral solution of +5 arsenic, so that the concentration of +5 arsenic is kept constant while that of hydrochloric acid is varied, produces the effect shown by the succeeding curves of this figure. The waves are nearly completely suppressed even in 10.2 *M* acid (Fig. 5e), and absent altogether from 9 *M* acid (Fig. 5f). No reduction wave was found either in a hydrochloric acid–perchloric acid medium containing 10.7 *M* hydrogen ion and 7.7 *M* chloride ion, or in a hydrochloric acid–lithium chloride medium containing 8.2 *M* hydrogen ion and 11.2 *M* chloride ion. Evidently both hydrogen and chloride ions at very high activity are essential for the conversion of the +5 arsenic into the reducible species, which must be an ion in which some or all of the oxygen atoms of the arsenate ion have been replaced by chloride.

Though the increase of i_d/C with increasing concentration of +5 arsenic above about 0.4 m*M* is clearly disadvantageous in practical analytical work, no maximum suppressor has been found which eliminates this behavior without causing a severe distortion of the entire polarogram.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Thermodynamics of the Neptunium(IV) Sulfate Complex Ions

BY J. C. SULLIVAN AND J. C. HINDMAN

RECEIVED JUNE 9, 1954

The extraction of neptunium(IV) into benzene with the chelating agent, thenoyltrifluoroacetone, has been used to demonstrate the existence of the +4 ion of neptunium in acid perchlorate solution. This +4 ion of neptunium has been shown to associate with sulfate in perchloric acid solution at an ionic strength of 2.00 according to the reactions $Np^{+4}(aq.) + HSO_4^- = NpSO_4^{++} + H^+$, $NpSO_4^{++} + HSO_4^- = Np(SO_4)_2 + H^+$. The association constants for the stepwise reactions at 25° are $k_1 = 270 \pm 27$ and $k_2 = 11.0 \pm 2.2$. The partial molal heat changes for the reactions are, respectively, -1.17 ± 0.16 and $+3.64 \pm 1.02$ kcal./mole. The corresponding partial molal entropy changes are 7.2 ± 0.6 and 18.7 ± 3.6 e.u.

Studies of the distribution of a metal cation between an aqueous and a benzene phase with the aid of the chelating agent, thenoyltrifluoroacetone, have proved extremely useful in determining both the charge on a metal ion in the absence of a complexing ligand and the association constants in complexing media.[1,2] This method has been used in the present paper to definitely establish the existence of the Np^{+4}(aq.) ion as the predominant species in perchloric acid solution.

The measurements have been extended to a study of the association behavior of Np^{+4} (aq.) in sulfate media. In order to determine the factors affecting the association with this ligand, calculations of the heat and entropy changes involved in the association process have been made from measurements of the temperature dependence of the equilibrium constants.

Experimental

A. Materials.—The perchloric acid was G. Frederick Smith, reagent grade double-vacuum distilled standardized against NaOH. The sodium perchlorate was prepared from perchloric acid and sodium carbonate and twice recrystallized from distilled water. Solutions were prepared on a weight basis. The sulfuric acid was reagent grade assayed both for total sulfate and for acidity. The thenoyl trifluoracetone (abbreviated TTA, hereafter) was a product of the Dow Chemical Co. The TTA solutions were made by weighing a given amount of the solid into a known volume of benzene. The Np(IV) was prepared by the method of Cohen and Hindman.[3]

B. Procedure.—The total ionic strength was kept constant at 2.00 by use of sodium perchlorate and perchloric acid. For the sulfate studies the acidity was kept constant at 2.00 *N*. Two ml. of aqueous and benzene solutions were pipetted into 10-ml. erlenmeyer flasks fitted with ground glass stoppers. The stoppers were waxed and the flasks were then covered with special rubber containers. The covered vessels were agitated in a constant temperature water-bath until equilibrium was reached. It was found that the same equilibrium was attained if a concentrated solution of the neptunium(IV) chelate in benzene was agitated with a perchloric acid solution as when a perchloric acid solution of neptunium(IV) was agitated with a benzene phase containing the chelating agent, thus demonstrating the reversibility of the system. Duplicate aliquots of each layer were mounted on Pt plates and radiochemically assayed using a methane proportional counter. These duplicate assays checked to within the statistical accuracy of the counting, ±0.5%. Duplicate samples checked to within ±1%. The isotope of neptunium was the long lived α-emitter, Np^{237}.

Results and Discussions

Formula of the TTA Complex of Neptunium Extracted into Benzene.—As Connick and McVey[1] have pointed out, the first step in the process of studying complex formation by the TTA method is the assignment of the formula of the metal ion complex extracted into the benzene layer and the determination of the degree of complex formation by the chelating species in the aqueous phase. A general equation for the reactions between Np(IV) and TTA may be written

$$(Np(OH)_iB_j)^{+4-i-j} + (p-j)HB = Np(OH)_{4-p}B_p + (4-i-j)H^+ + (i+p-4)H_2O \quad (1)$$

where HB is used to represent undissociated TTA. In the following equations, brackets are used to indicate concentrations of the enclosed species.

$[Np(OH)_iB_j{}^{+4-i-j}]$ = complexed species in aqueous phase
$[Np(OH)_{4-p}B_p]$ = complexed species in benzene phase[4]

The extraction coefficient may be defined as

$$E = \frac{\sum\limits_p [Np(OH)_{4-p}B_p]}{\sum\limits_i \sum\limits_j [Np(OH)_iB_j{}^{+4-i-j}]} \quad (2)$$

---

(1) R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

(2) R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

(3) D. Cohen and J. C. Hindman, *ibid.*, **74**, 4679 (1952).

(4) The possible species in the benzene layer are subject to the requirement that only neutral molecules be present and limited by the maximum coördination number of the neptunium(IV) which is considered to be 8 for oxygen.

It can be readily shown from equations 1 and 2 that if the Np(IV) is chelated with 4 molecules of TTA in the benzene phase ($p = 4$) and no chelate complex is formed in the aqueous layer ($j = 0$), then

$$\log E' = 4 \log \text{HB} \quad (3)$$

where E' is defined by the equation

$$E' = E\gamma_{\text{NpB}_4} \quad (4)$$

To compute E' from the measured extraction coefficient, E, it is necessary to assume that the activity coefficients of all neptunium species in the benzene layer are equal to γ_{NpB_4} which is in turn assumed to be $\gamma_{\text{NpB}_4} = \gamma_{\text{UB}_4}$. γ_{UB_4} has been determined by Reas[5a] and found to be equal to γ_{HB}.[5b]

The dependence of E on HB concentration at various temperatures and 2.00 M $HClO_4$ are given in Table I.

TABLE I

THE DEPENDENCE OF THE EXTRACTION COEFFICIENT E' ON THE CONCENTRATION OF THENOYLTRIFLUOROACETONE

$[H^+] = 2.00$, $\mu = 2.00$, Np(IV) $\cong 1 \times 10^{-4}$ M (initial aqueous)

10.2 ± .2°		25.2 ± .2°		35.3 ± .2°	
log E'	log [HB]	log E'	log [HB]	log E'	log [HB]
+0.713	−0.936	1.391	−0.620	+1.010	−0.784
+ .387	−1.057	1.263	− .745	+ .712	− .852
− .539	−1.285	1.013	− .827	+ .516	− .932
−1.271	−1.444	.781	− .890	+ .317	−1.045
−1.402	−1.481	.754	− .900	+ .171	−1.072
−1.845	−1.586	.485	− .970	−1.316	−1.455
−2.188	−1.678	.0022	−1.111	−1.812	−1.584
−3.385	−1.959	− .646	−1.270	−2.239	−1.668
		−1.472	−1.480	−3.413	−1.960

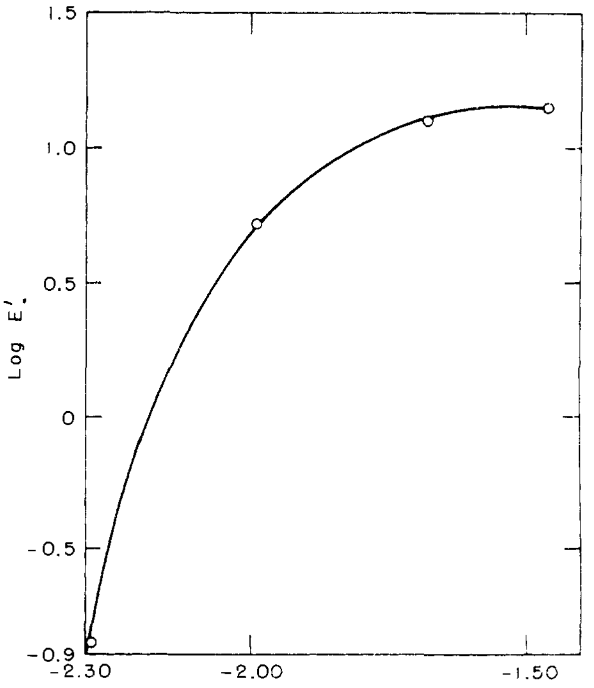

Fig. 1.—Dependence of extraction coefficient on TTA concentration at low acid; $\mu = 2.00$, $t = 25°$, $[H^+] = 0.2$ M.

Graphical analysis showed that a straight line with the slope of +4.0 fits the data up to an initial HB concentration of 0.1 M. Therefore, $j = 0$ and $p = 4$ and equation 2 may be rewritten in the form

$$E = \frac{[\text{NpB}_4]}{\sum_i [\text{Np(OH)}_i^{+4-i}]} \quad (5)$$

In the experiments in the following sections, the HB concentrations were adjusted so that the extraction was carried out in the region where the fourth power dependence of the extraction coefficient on HB was obeyed.

Formula of the Neptunium(IV) in Perchlorate Media.—Combining equations 1 and 5 with the equation for hydrolysis of Np^{+4}

$$\text{Np}^{+4}(\text{aq}) + i\text{H}_2\text{O} \rightleftharpoons \text{Np(OH)}_i^{+4-i} + i\text{H}^+ \quad (6)$$

and the previously developed equations[6] we have for the average number of OH^- groups, $\bar{n}$,[7] bound per neptunium(IV) ion

$$\bar{n} = -\frac{d \log E''}{d \log [\text{H}^+]} \quad (7)$$

where E'' is defined by the equation

$$E'' = E/[\text{HB}]^4[\gamma\text{HB}]^4$$

The data in Table II show that Np(IV) exists as an unhydrolyzed tetrapositive ion from 2.00 $M[H^+]$ to 0.51 M $[H^+]$. The deviation of the extraction curve from linearity at low acid suggests that hydrolysis of neptunium(IV) is occurring. A determination of the TTA dependence of the extraction coefficient at lower acidity, Fig. 1, shows marked deviation from the fourth power dependence on TTA concentration. This suggests that appreciable complex formation between the TTA and the neptunium(IV) is occurring in the aqueous phase. The low value of log E' suggests formation of complexes of the type $Np_j(OH)_iB_p$.

TABLE II

THE DEPENDENCE OF THE EXTRACTION COEFFICIENT, E'', ON THE CONCENTRATION OF HYDROGEN ION

$\mu = 2.00$ [Np(IV)] $= 1 \times 10^{-4}$ M (initial aqueous)

10.2 ± 0.2°		25.2 ± 0.2°	
log E''	log $[H^+]$	log E''	log $[H^+]$
4.354	0.297	4.484	0.279
4.499	.270	4.721	.225
5.013	.110	4.986	.158
5.263	.0719	5.551	.019
5.416	.0334	6.176	− .150
5.451	.0212	6.704	− .292
5.572	− .0114	6.750	− .323
6.054	− .130	6.948	− .414
6.344	− .201	7.238	− .470
6.981	− .437	7.310	− .539
7.101	− .527	7.433	− .611
7.175	− .699	7.552	− .711
7.265	− .819	7.740	− .824

Although the experiments were run under conditions such that the formation of polynuclear species would be minimized (Σ[Np(IV)] low) it was considered desirable to specifically test this point.

---

[5] (a) W. H. Reas, unpublished work; (b) E. L. King and W. H. Reas, THIS JOURNAL, **73**, 1804 (1951).

[6] J. C. Sullivan and J. C. Hindman, *ibid.*, **74**, 6091 (1952).

[7] J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941.

In the event polynuclear species are formed equation 5 would be written as

$$E = \frac{[\mathrm{NpB_4}]}{\sum\limits_m \sum\limits_i [\mathrm{Np}_m(\mathrm{OH})_i{}^{+4m-i}]} \tag{5a}$$

It is therefore possible to determine whether polynuclear complex formation occurs by studying the variation of E with metal ion concentration. At constant acidity, ionic strength and HB activity, the extraction coefficient should be independent of the metal ion concentration in the absence of polynuclear complex formation. Table III, containing data at two temperatures in 2.00 M $HClO_4$, shows that no polynuclear species are formed up to neptunium concentrations of 3×10^{-3} M.

TABLE III

THE DEPENDENCE OF THE EXTRACTION COEFFICIENT, E'', ON THE NEPTUNIUM(IV) CONCENTRATION

$[H^+] = 2.00$, $\mu = 2.00$.

25.2 ± 0.2° log E''	M $[Np^{+4}]$ initial aqueous	10.2 ± 0.2° log E''	M $[Np^{+4}]$ initial aqueous
4.448 ± 0.008	3.04×10^{-4}	4.551 ± 0.009	1.35×10^{-4}
4.452 ± .009	1.52×10^{-3}	4.559 ± .008	1.35×10^{-3}
4.459 ± .005	3.04×10^{-3}	4.571 ± .010	2.74×10^{-3}

The Sulfate Complexes of Neptunium(IV).—On addition of sulfate ion to perchloric acid solutions of neptunium(IV), the extraction coefficient becomes

$$E = \frac{\sum\limits_x [\mathrm{NpB}_{4-2x}(\mathrm{SO_4})_x]}{\sum\limits_m \sum\limits_x \sum\limits_y [\mathrm{Np}_m(\mathrm{SO_4})_x\mathrm{B}_y{}^{+4-2x-y}]} \tag{8}$$

if cognizance is taken of the possibility of polynuclear complex formation in the aqueous phase as well as the formation of heterogeneous extractable species.

To eliminate the variables in equation 8 in a systematic fashion as has been done previously in the establishment of the charge on the neptunium(IV) ion, a study was first made of the variation of E as a function of the TTA concentration. The results are tabulated in Table IV. These experiments covered the range of TTA concentrations that preliminary experiments indicated would be required in order to secure reasonable extraction in the presence of the anion.

TABLE IV

THE VARIATION IN THE EXTRACTION COEFFICIENT, E'', AS A FUNCTION OF THE TTA CONCENTRATION

$\mu = 2.00$, $[H^+] = 2.00$, initial $[Np(IV)] = 1.35 \times 10^{-4}$ M.

0.498 M $[HSO_4^-]$ 10.2 ± 0.2° log E''	log [HB]	0.00920 M $[HSO_4^-]$ 25.2 ± 0.2° log E''	log [HB]	0.0498 M $[HSO^-]$ 35.3 ± 0.2° log E''	log [HB]
−0.790	−1.039	−0.141	−1.050	−2.550	−1.440
− .332	−0.936	+0.332	−0.929	−1.121	−1.071
− .039	−0.858	+0.734	−0.830	−1.019	−1.045
+ .249	−0.778	+1.042	−0.747	−0.580	−0.941
+ .535	−0.699	+1.330	−0.669	−0.295	−0.867
				+0.022	−0.794
				+0.389	−0.711

As these data show, no heterogeneous species involving Np(IV) and TTA exist in either the benzene or aqueous phases and therefore equation 8 can be simplified to

$$E = \frac{[\mathrm{NpB_4}]}{\sum\limits_m \sum\limits_y [\mathrm{Np}_m(\mathrm{SO_4})_y{}^{+4-2y}]} \tag{9}$$

To further reduce the variables, the extraction coefficient was investigated as a function of the Np(IV) concentration. The data in Table V show that no polynuclear species of neptunium and sul-

TABLE V

THE DEPENDENCE OF THE EXTRACTION COEFFICIENT, E'', ON THE NEPTUNIUM(IV) CONCENTRATION

10.2 ± 0.2° 0.0499 M $[HSO_4^-]$ log E''	M $[Np^{+4}]$ initial aqueous	25.2 ± 0.2° 0.00920 M $[HSO_4^-]$ log E''	M $[Np^{+4}]$ initial aqueous
3.484 ± 0.007	1.62×10^{-4}	4.124 ± 0.004	3.04×10^{-4}
3.481 ± .008	1.10×10^{-3}	4.104 ± .018	1.52×10^{-3}
3.493 ± .010	2.29×10^{-3}	4.095 ± .015	3.04×10^{-3}

TABLE VI

VARIATION OF THE EXTRACTION COEFFICIENT, E'', WITH BISULFATE CONCENTRATION

$\mu = 2.00$, $[H^+] = 2.00$, $[Np(IV)] = 1 \times 10^{-4}$ (initial aqueous)

10.2 ± 0.2° log $[HSO_4^-]$	log E''	25.2 ± 0.2° log $[HSO_4^-]$	log E''	35.3 ± 0.2° log $[HSO_4]^-$	log E''
−3.126	4.452	−3.340	4.483	−3.126	4.306
−2.825	4.417	−3.144	4.438	−2.832	4.279
−2.649	4.380	−3.039	4.423	−2.825	4.278
−2.524	4.344	−2.780	4.402	−2.649	4.224
−2.427	4.309	−2.641	4.372	−2.524	4.192
−2.348	4.294	−2.626	4.339	−2.427	4.160
−2.281	4.246	−2.516	4.364	−2.348	4.099
−2.223	4.228	−2.479	4.323	−2.281	4.085
−2.172	4.196	−2.456	4.340	−2.223	4.086
−2.126	4.181	−2.445	4.321	−2.172	4.026
−2.047	4.140	−2.340	4.283	−2.126	4.004
−1.980	4.088	−2.325	4.253	−2.047	3.953
−1.922	4.044	−2.155	4.171	−1.980	3.915
−1.871	4.020	−2.144	4.164	−1.922	3.870
−1.825	3.982	−2.081	4.159	−1.871	3.820
−1.746	3.933	−1.991	4.066	−1.825	3.804
−1.649	3.839	−1.927	4.053	−1.750	3.704
−1.603	3.798	−1.817	3.980	−1.649	3.615
−1.570	3.779	−1.794	3.905	−1.603	3.565
−1.503	3.706	−1.780	3.888	−1.570	3.529
−1.445	3.673	−1.757	3.901	−1.503	3.444
−1.399	3.601	−1.704	3.833	−1.445	3.387
−1.394	3.586	−1.624	3.754	−1.432	3.386
−1.349	3.551	−1.516	3.638	−1.399	3.363
−1.302	3.468	−1.456	3.562	−1.394	3.338
−1.188	3.330	−1.431	3.540	−1.348	3.257
−1.098	3.216	−1.403	3.533	−1.302	3.206
−1.001	3.058	−1.357	3.447	−1.188	3.076
− .940	2.943	−1.341	3.454	−1.098	2.959
− .887	2.860	−1.283	3.379	−1.001	2.841
− .825	2.788	−1.276	3.355	−0.940	2.734
		−1.173	3.242	− .887	2.665
		−1.166	3.263	− .825	2.559
		−1.122	3.172		
		−1.106	3.151		
		−1.089	3.132		
		−1.058	3.090		
		−1.054	3.047		
		−1.039	3.044		
		− .994	2.972		
		− .901	2.752		

fate are present in the aqueous phase hence equation 9 reduces to

$$E = \frac{[NpB_4]}{\sum_y [Np(SO_4)_y{}^{+4-2y}]} \qquad (10)$$

Table VI summarizes the experimental study of E'' as a function of bisulfate concentration at constant acidity and ionic strength and corrected to unit activity in the benzene phase. Since $\bar{n}$ shows a maximum of 1.7, we conclude that under the present experimental conditions only two complexes are involved.[6]

Writing the reactions for the successive steps as

$$Np^{+4} + HSO_4^- \rightleftarrows NpSO_4^{++} + H^+ \qquad (11)$$

$$k_1 = \frac{[H^+][NpSO_4^{++}]}{[Np^{+4}][HSO_4^-]} \qquad (12)$$

$$NpSO_4^{++} + HSO_4^- \rightleftarrows Np(SO_4)_2 + H^+ \qquad (13)$$

$$k_2 = \frac{[H^+][Np(SO_4)_2]}{[NpSO_4^{+2}][HSO_4^-]} \qquad (14)$$

the constants were calculated from the data in Table VI by the method of Leden.[6] It should be noted that for the experimental conditions the approximation ($\Sigma(HSO_4^-) = [HSO_4^-]$ free) is valid. The smooth curve in Fig. 2 was calculated from the constants tabulated in Table VII in the form $[k_1/H^+]$ and $[k_2/H^+]$. The limits of error indicated in Table VII were estimated from the scattering of the experimental data in the Leden F ([A]) plot[6] used to calculate the constants of the systems.

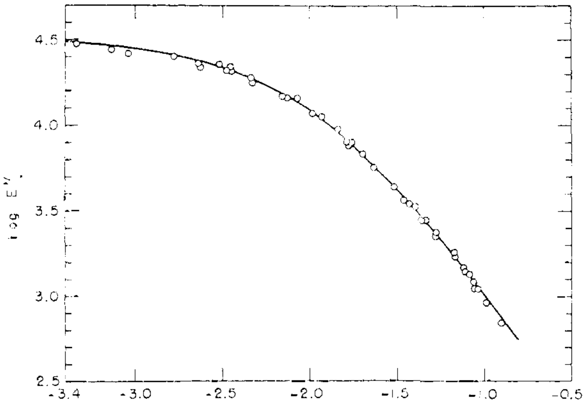

Fig. 2.—Dependence of extraction coefficient, E'', on concentration of $[HSO_4^-]$: solid line, calculated curve; $\mu = 2.00$, $[H^+] = 2.00$, $t = 25°$.

TABLE VII

CONSTANTS FOR THE STEPWISE ASSOCIATION OF Np^{+4} AND HSO_4^-

	10.2 ± 0.2°	25.2 ± 0.2°	35.3 ± 0.2°
k_1	296 ± 30	270 ± 27	250 ± 25
k_2	8.11 ± 1.62	11.0 ± 2.2	13.7 ± 2.7

The Heat and Entropy Changes in the Complexing Reaction.—From the temperature dependence of the association constants the partial molal heat and entropy changes for reactions 11 and 13 have been calculated. Those are summarized in Table VIII. The errors in the heat changes were estimated by the familiar method of the "Propagation of Errors." It should be noted that the maximum possible errors are considerably larger. The errors in ΔS were estimated from the errors in the ΔH values.

TABLE VIII

VALUES FOR FREE ENERGY, HEAT AND ENTROPY CHANGE FOR THE REACTIONS OF BISULFATE AND NEPTUNIUM(IV)

Reaction	ΔF, kcal./mole	ΔH, kcal./mole	ΔS, e.u.
$Np^{+4} + HSO_4^- \rightleftarrows NpSO_4^{++} + H^+$	−3.32	−1.17 ± 0.16	7.2 ± 0.6
$NpSO_4^{+2} + HSO_4^- \rightleftarrows Np(SO_4)_2 + H^+$	−1.92	3.64 ± 1.02	18.7 ± 3.6

The factors of importance in the complexing of neptunium(IV) by sulfate can be more readily seen if the reactions are put in the form

$$Np^{+4} + SO_4^{=} \rightleftarrows NpSO_4^{++} \qquad (15)$$

$$NpSO_4^{++} + SO_4^{=} \rightleftarrows Np(SO_4)_2 + H^+ \qquad (16)$$

A value of 0.084 for the dissociation constant of bisulfate ion has been reported[8] for a medium of the ionic strength used. Combining this with the value of −5,200 cal. for the heat of dissociation of bisulfate[9] we calculate for reaction 15, $\Delta F = -4.79$ kcal./mole, $\Delta H = +4.0$ kcal./mole and $\Delta S = 29.5$ cal. deg.$^{-1}$ and for reaction 16, $\Delta F = -3.39$ kcal./mole, $\Delta H = 6.22$ kcal./mole and $\Delta S = 41.0$ cal. deg.$^{-1}$. It can be clearly seen that the reactions proceed only because of the entropy changes. The positive values for the heats point out that it would be particularly inappropriate in the present case to use the free energy as an index of bond strength.

---

[8] E. L. Zebroski, H. W. Alter and F. K. Heumann, THIS JOURNAL, **73**, 5646 (1951).

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 430.