densities on the surfaces, which would lead to a higher mobility.

The method of Dye and Spedding[4] was applied to the data for the 3-1 and 1-3 electrolytes. It was possible to fit the data up to 4 to 16 × $10^{-4}$ $N$. The $\mathring{a}$ values required are: $Co(en)_3(NO_3)_3$, 3.23; $Co(pn)_3(ClO_4)_3$, 3.47; $K_3Co(CN)_6$, 3.80. These values are too small but are of the same order of magnitude as those required to fit activity data. It is apparent that in both cases all of the inadequacies of present theory are being absorbed by the single parameter $\mathring{a}$, and it is not surprising that the "adjusted ionic size" is not its actual size. However, this calculation serves to emphasize the fact that these higher terms are *not* negligible.

Association "constants" were calculated as described in the paper which follows.[15] The value of the association constant required to fit the data varied considerably with concentration, indicating that ion-pair formation alone is unable to account for the conductance behavior. Typically, a tenfold concentration decrease from 3 × $10^{-3}$ $N$ to 3 × $10^{-4}$ N required a 100% or more increase in the association constant. This undoubtedly is due to lack of knowledge of the conductance to be expected for a completely ionized unsymmetrical electrolyte.

While current theory is inadequate, it is hoped that data such as these for a number of different unsymmetrical electrolytes will serve as a guide for the development of a satisfactory theory for dilute solutions of high-charge salts.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

# Activity Coefficients and Conductances of High-charge (4-1, 1-4, 1-2) Electrolytes. II.[1a]

BY KENNETH O. GROVES, JAMES L. DYE AND CARL H. BRUBAKER, JR.[1b]

RECEIVED AUGUST 27, 1959

Mean activity and osmotic coefficients of aqueous solutions of $Pt(pn)_3Cl_4$, $[NMe_4]_4Mo(CN)_8$, $K_4W(CN)_8$ and $K_2Pt(CN)_4$ were determined at 25° by isopiestic comparison with aqueous KCl solutions. The Debye–Hückel equation plus a linear term in concentration fit the data at low concentrations. Conductivity measurements were made with solutions of the four electrolytes and decided deviations from the Onsager limiting law were observed. The behavior of these unsymmetrical electrolytes and relationship to present theory is discussed.

The present work is a continuation of a program of investigation of the properties of solutions of high-charge electrolytes. Previously we have described the studies of a number of 4-1, 1-4, 3-1, 1-3 and 3-2 electrolytes.[2,3]

The compounds investigated in this work were tris-(1,2-diaminopropane)-platinum(IV) chloride monohydrate, tetramethylammonium octacyanomolybdate(IV) dihydrate, potassium octacyanotungstate(IV) dihydrate and potassium tetracyanoplatinate(II). Activity coefficients have been determined by the isopiestic method[2] and conductances were measured in line with our attempts to systematize the behavior of unsymmetrical electrolytes and to compare the results with existing theoretical treatments.

## Experimental

**Materials.**—Conductivity water was prepared as described in the preceding paper.[4]

Potassium tetracyanoplatinate (II), $K_2Pt(CN)_4$, was prepared by the method of Knop and Schedermann.[5] Purification was effected by fractional crystallization. The product thus obtained was the colorless $K_2Pt(CN)_4 \cdot 3H_2O$. The yellow anhydrous salt was obtained by drying the hydrated salt in an oven overnight at 100°. The anhydrous salt was kept desiccated during storage since it slowly becomes hydrated in the air. However, hydration is not rapid, and the salt can be weighed in the air.

Tris-(1,2-diaminopropane)-platinum(IV) chloride monohydrate, $Pt(pn)_3Cl_4 \cdot H_2O$, was prepared by the method of Smirnoff.[6] The crude chloride was purified by fractional crystallization. Later, quantities of this salt were purified by precipitation as the oxalate, recrystallization in this form and reconversion to the chloride by reaction with calcium chloride as described by Dwyer and Garvan.[7] This latter method was found to be a much more efficient procedure.

Tetramethylammonium octacyanomolybdate(IV) dihydrate, $[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$, was prepared by a quantitative metathesis reaction between $Ag_4[Mo(CN)_8] \cdot 2H_2O$ and $N(Me)_4Br$. $Ag_4[Mo(CN)_8] \cdot 2H_2O$ was prepared from $K_4[Mo(CN)_8] \cdot 2H_2O$ by precipitation with silver nitrate. $K_4[Mo(CN)_8) \cdot 2H_2O$ was prepared and purified according to the directions given by Furman and Miller.[8] All of the above octacyanomolybdate salts were air dried.

Potassium octacyanotungstate(IV) dihydrate, $K_4W(CN)_8 \cdot 2H_2O$, was prepared and purified by the method of Olsson.[9]

The *p*H values of the solutions were determined and assured the absence of appreciable hydrolysis. Solutions were freshly prepared before each conductance run, and the lack of any time-dependence indicated stability of the solutions.

**Apparatus.**—The apparatus and experimental procedure used for the isopiestic measurements have been previously described.[2,10]

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[1] (a) This work is supported by the National Science Foundation under grants NSF-G9203 and NSF-G3288. (b) To whom correspondence should be directed.

[2] C. H. Brubaker, Jr., THIS JOURNAL, **78**, 5762 (1956); **79**, 4174 (1957).

[3] R. A. Wynveen, Ph.D. dissertation, Michigan State University (1959).

[4] R. A. Wynveen, J. L. Dye and C. H. Brubaker, Jr., THIS JOURNAL, **82**, 0000 (1960).

[5] "Gmelin's Handbuch der Anorganischen Chemie," Verlag Chemie, Weinheim Bergstrasse, Berlin, **68C**, 201 (1940).

[6] *Ibid.*, **68D**, 475 (1957).

[7] F. P. Dwyer and F. L. Garvan, THIS JOURNAL, **81**, 1043 (1959).

[8] N. H Furman and C. O. Miller, "Inorganic Syntheses," Vol. III, ed. by L. F. Audrieth, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 160.

[9] O. Z. Olsson, *Z. anorg. Chem.*, **88**, 50 (1914).

[10] C. H. Brubaker, Jr., C. E. Johnson, C. P. Knop and F. Betts, *J. Chem. Educ.*, **34**, 42 (1957).

The apparatus and experimental procedure for conductance measurements were the same as those described in the preceding paper.[4]

Molal concentrations were converted to molar concentrations with the aid of densities measured for each standard solution at concentrations up to about 0.02 *m*. Within experimental error the densities are described by the equation

$$\rho = 0.9971 + Am \qquad (1)$$

The values of $A$ are: $K_4W(CN)_8$, 0.8784; $[N(Me)_4]_4Mo(CN)_8$, 0.1080; $Pt(pn)_3Cl_4$, 0.3155; $K_2Pt(CN)_4$, 0.2514.

## Results and Discussion

**Activity Coefficients.**—The experimental molalities and osmotic coefficients are given in Table I. The calculations of activity coefficients were made as in previous work,[2] either by the method of Scatchard and Prentiss[11] and Smith,[12] involving the use of the extended Debye–Hückel equation

$$1 - \phi = 0.7676\, S_{m(f)}\, \sigma_m\, m^{1/2} + \frac{1}{2} B_m \qquad (2)$$

or by graphical integration of the Gibbs–Duhem equation according to

$$\ln \gamma_{\pm} = -(1 - \phi) - 2 \int_0^m \frac{(1 - \phi)}{m^{1/2}}\, dm^{1/2} \qquad (3)$$

Extrapolation of the data to infinite dilution, for (3), was done with the Debye–Hückel equation involving only the parameter $\mathring{a}$.

TABLE I

EXPERIMENTAL OSMOTIC COEFFICIENTS FOR $K_4W(CN)_8 \cdot 2H_2O$, $[N(CH_3)_4]_4Mo(CN)_8 \cdot 2H_2O$, $Pt(pn)_3Cl_4 \cdot H_2O$ AND $K_2Pt(CN)_4$ AT 24.978 ± 0.005°

| $K_4W(CN)_8 \cdot 2H_2O$ | | $[N(CH_3)_4]_4Mo(CN)_8 \cdot 2H_2O$ | |
|---|---|---|---|
| $m$ | $\phi$ obsd. | $m$ | $\phi$ obsd. |
| 0.06593 | 0.6588 | 0.05441 | 0.6218 |
| .0773 | .6517 | .1039 | .5843 |
| .1081 | .6288 | .2003 | .5571 |
| .1096 | .6238 | .3806 | .5201 |
| .2238 | .5803 | .4478 | .5228 |
| .2624 | .5678 | .4551 | .5193 |
| .3550 | .5533 | .5505 | .5304 |
| .3950 | .5523 | .6390 | .5383 |
| .4320 | .5497 | .7241 | .5489 |
| .4912 | .5414 | .8510 | .5625 |
| .5249 | .5417 | 1.0751 | .5917 |
| .5996 | .5347 | 1.1505 | .5987 |
| .8023 | .5376 | 1.2355 | .6138 |
| 1.0630 | .5510 | 1.3384 | .6192 |
| 1.2856 | .5744 | 1.4588 | .6299 |
| 1.5452 | .6109 | | |
| $K_2Pt(CN)_4$ | | $Pt(pn)_3Cl_4 \cdot H_2O$ | |
| $m$ | $\phi$ obsd. | $m$ | $\phi$ obsd. |
| 0.05922 | 0.8745 | 0.05588 | 0.6719 |
| .07249 | .8697 | .06652 | .6546 |
| .1145 | .8494 | | |
| .2706 | .8189 | .06783 | .6517 |
| .3524 | .8146 | .08311 | .6350 |
| .3704 | .8108 | .1047 | .6191 |
| .4722 | .7980 | | |
| .5494 | .7962 | | |
| .6631 | .7892 | | |
| .7277 | .7841 | | |
| .7613 | .7759 | | |
| .9150 | .7699 | | |
| .9481 | .7686 | | |

The first method was used to determine the activity coefficients for $Pt(pn)_3Cl_4$ and for the evaluation of $\mathring{a}$ and $B$ for the other electrolytes reported here using data up to approximately 0.2 *m*. However, at concentrations larger than this the deviation from equation 1 becomes large. Therefore, graphical integration based on equation 2 was used to calculate the activity coefficients for the electrolytes $K_4W(CN)_8$, $[N(Me)_4]_4Mo(CN)_8$ and $K_2Pt(CN)_4$ and values of $\mathring{a}$ for all salts. In Table II are listed the resulting activity coefficients at rounded values of the concentrations.

TABLE II

SMOOTHED ACTIVITY AND OSMOTIC COEFFICIENTS AT 25°

| | $K_4W(CN)_8 \cdot 2H_2O$ | | $[N(Me)_4]_4Mo(CN)_8 \cdot 2H_2O$ | |
|---|---|---|---|---|
| $m$ | $\gamma_{\pm}$ | $\phi$ | $\gamma_{\pm}$ | $\phi$ |
| 0.01 | 0.419 | 0.854 | 0.359 | 0.753 |
| .025 | .295 | .768 | .252 | .685 |
| .050 | .216 | .683 | .184 | .638 |
| .075 | .180 | .651 | .155 | .612 |
| .10 | .159 | .632 | .136 | .596 |
| .25 | .111 | .572 | .0859 | .542 |
| .50 | .0808 | .541 | .0612 | .524 |
| .75 | .0653 | .536 | .0515 | .551 |
| 1.00 | .0578 | .548 | .0468 | .581 |
| 1.10 | .0537 | .555 | .0451 | .592 |
| 1.25 | .0515 | .571 | .0440 | .610 |
| 1.44 | | | .0426 | .631 |
| 1.50 | .0478 | .604 | | |
| | $Pt(pn)_3Cl_4 \cdot H_2O$ | | $K_2Pt(CN)_4$ | |
| 0.01 | .0429 | 0.786 | 0.756 | 0.937 |
| .025 | .330 | .737 | .672 | .907 |
| .050 | .258 | .683 | .612 | .882 |
| .075 | .213 | .643 | .573 | .867 |
| .10 | .177 | .621 | .545 | .857 |
| .25 | | | .470 | .823 |
| .50 | | | .402 | .795 |
| .75 | | | .365 | .782 |
| 1.00 | | | .337 | .768 |

The values of the activity coefficients do not vary significantly with the method used. However, the parameter $\mathring{a}$ depends upon the method employed (Table III).

TABLE III

CALCULATED VALUES FOR THE PARAMETERS OF THE EXTENDED DEBYE–HÜCKEL EQUATION FOR MEAN MOLAL ACTIVITY COEFFICIENTS

| Electrolyte | $B$[a] | $\mathring{a}$[a] | $\mathring{a}$[b] |
|---|---|---|---|
| $K_4W(CN)_8$ | 2.40 | 7.09 | 4.81 |
| $[N(Me)_4]_4Mo(CN)_8$ | 2.52 | 4.84 | 4.25 |
| $Pt(pn)_3Cl_4$ | 4.24 | 8.11 | 5.17 |
| $K_2Pt(CN)_4$ | 1.36 | 7.18 | 6.19 |

[a] Calculated using equation 1. [b] Calculated by fitting the Debye–Hückel equation to the data at lowest concentrations with equation 3.

The magnitudes of the activity coefficients listed in Table II are similar to those previously reported for electrolytes of the 1–4, 4–1 charge type.[2,13] However, those derived for $K_2Pt(CN)_4$ lie between those for typical 1-1 and 1-2 electrolytes. One possible explanation for this may be that the square planar structure of the $Pt(CN)_4^{-2}$ ion allows ion-

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(11) G. Scatchard and S. S. Prentiss, THIS JOURNAL, **55**, 4355 (1933).

(12) R. P. Smith, *ibid.*, **61**, 500 (1939).

(13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 566.

TABLE IV

EXPERIMENTALLY DETERMINED CONDUCTANCES IN AQUEOUS SOLUTION AT 25°

A. $K_4W(CN)_8$

| Concn. ($N \times 10^3$) | Run no. | Eq. conduct. ($\Lambda$) |
|---|---|---|
| 0.33052 | 2 | 180.79 |
| 0.49450 | 1 | 178.16 |
| 0.62008 | 2 | 176.42 |
| 1.0252 | 2 | 172.04 |
| 1.1304 | 1 | 171.23 |
| 1.8984 | 1 | 165.88 |
| 2.5052 | 1 | 162.51 |
| 3.4308 | 1 | 158.41 |
| 4.6416 | 2 | 153.31 |
| 4.8724 | 1 | 153.43 |
| 7.4252 | 1 | 146.70 |
| 9.3191 | 2 | 142.87 |
| 10.521 | 3 | 142.09 |
| 20.680 | 3 | 130.22 |
| 44.482 | 3 | 117.97 |
| 90.401 | 3 | 107.61 |
| 191.84 | 3 | 97.32 |
| 401.16 | 3 | 90.55 |

| Run no. | $L_{H_2O} \times 10^6$ | Cell constant |
|---|---|---|
| 1 | 1.290 | 1.0322 |
| 2 | 0.6028 | 1.0365 |
| 3 | [a] | 30.00 |

RMS deviation 0.11 conductance unit

B. $[N(Me)_4]_4Mo(CN)_8$

| Concn. ($N \times 10^3$) | Run no. | Eq. conduct. ($\Lambda$) |
|---|---|---|
| 0.30776 | 2 | 146.47 |
| 0.42880 | 1 | 144.04 |
| 0.68812 | 1 | 139.84 |
| 1.0007 | 2 | 136.12 |
| 1.0681 | 1 | 135.15 |
| 1.4437 | 1 | 131.32 |
| 2.1498 | 1 | 125.64 |
| 2.9850 | 1 | 119.92 |
| 3.9924 | 1 | 114.91 |
| 6.2040 | 1 | 107.06 |
| 6.4376 | 2 | 106.56 |
| 8.4879 | 2 | 101.29 |
| 11.093 | 2 | 96.06 |
| 12.044 | 3 | 93.50 |
| 27.348 | 3 | 76.82 |
| 56.212 | 3 | 65.67 |
| 106.52 | 3 | 56.04 |
| 208.36 | 3 | 47.04 |

| Run no. | $L_{H_2O} \times 10^6$ | Cell constant |
|---|---|---|
| 1 | 1.095 | 1.0322 |
| 2 | 1.134 | 1.0322 |
| 3 | [a] | 30.00 |

RMS deviation 0.15 conductance unit

C. $K_2Pt(CN)_4$

| Concn. ($N \times 10^3$) | Run no. | Eq. conduct. ($\Lambda$) |
|---|---|---|
| 0.12024 | 1 | 152.55 |
| .12834 | 2 | 152.50 |
| .35512 | 1 | 150.83 |
| .39296 | 2 | 150.51 |
| .75512 | 2 | 149.08 |
| .79274 | 1 | 148.97 |
| 1.0509 | 2 | 148.11 |
| 1.2740 | 1 | 147.53 |
| 1.7572 | 2 | 146.51 |
| 2.1874 | 1 | 145.69 |
| 2.8680 | 1 | 144.54 |
| 4.0492 | 1 | 142.87 |
| 4.2714 | 3 | 142.11 |
| 5.8924 | 3 | 140.66 |
| 7.2285 | 3 | 139.19 |
| 9.2200 | 4 | 138.07 |
| 16.448 | 4 | 133.94 |
| 24.160 | 4 | 131.36 |
| 89.380 | 4 | 119.87 |

| Run no. | $L_{H_2O} \times 10^6$ | Cell constant |
|---|---|---|
| 1 | 0.531 | 1.0365 |
| 2 | .631 | 0.3165 |
| 3 | .773 | 1.0319 |
| 4 | [a] | 30.00 |

RMS deviation 0.058 conductance unit

D. $Pt(pn)_3Cl_4$

| Concn. ($N \times 10^3$) | Run no. | Eq. conduct. ($\Lambda$) |
|---|---|---|
| 0.19206 | 2 | 154.81 |
| .33799 | 2 | 150.50 |
| .35367 | 1 | 150.49 |
| .51092 | 2 | 147.31 |
| .62696 | 1 | 145.23 |
| .63168 | 2 | 145.21 |
| .88432 | 2 | 141.77 |
| 1.0676 | 1 | 139.66 |
| 1.6810 | 1 | 133.66 |
| 2.6720 | 1 | 127.51 |
| 3.7531 | 1 | 122.91 |
| 5.9292 | 3 | 117.55 |
| 8.7320 | 3 | 113.39 |
| 19.218 | 3 | 101.69 |
| 27.344 | 3 | 95.55 |
| 54.044 | 3 | 84.17 |

| Run no. | $L_{H_2O} \times 10^6$ | Cell constant |
|---|---|---|
| 1 | 0.584 | 1.0365 |
| 2 | 0.612 | 0.3146 |
| 3 | [a] | 29.19 |

RMS deviation 0.086 conductance unit

[a] Variable; measurements made on separate solutions; water conductance measured for each stock.

ion interaction or ion-solvent interaction at the octahedral apexes which are not occupied by ligand groups.

**Conductivity.**—The measured equivalent conductances and the standard deviations from a smooth curve are given in Table IV.

The steep slopes observed in the phoreograms, as infinite dilution is approached, would appear to introduce considerable uncertainty in the evaluation of the limiting conductances, $\Lambda^0$, by a simple linear extrapolation procedure.

In the case of 1-1 electrolytes in water, a common procedure[14] is to extrapolate a graph of $\Lambda^{0\prime}$ *vs.* $C$ to infinite dilution, in which

$$\Lambda^{0\prime} = \frac{\Lambda + \beta^* C^{1/2}}{1 - \alpha^* C^{1/2}} \qquad (4)$$

the symbols are these of Harned and Owen.[13] Such a graph is unsatisfactory for many unsymmetrical electrolytes because of the deep minima involved.

The observed phoreograms for these electrolytes could be fit *up to the minimum only* by the Owen method[15] using the extended Onsager equation

$$\Lambda^{0\prime\prime} \equiv \Lambda + S_\Lambda N^{1/2} = \Lambda^0 + AN \log N + BN \qquad (5)$$

The parameters $A$, $B$ and $\Lambda^0$ required to fit the data are given in Table V. The deviations from the simple Onsager equation are plotted as $\Lambda^{0\prime\prime} - \Lambda^0$ in Fig. 1. The solid lines are calculated by equation 5.

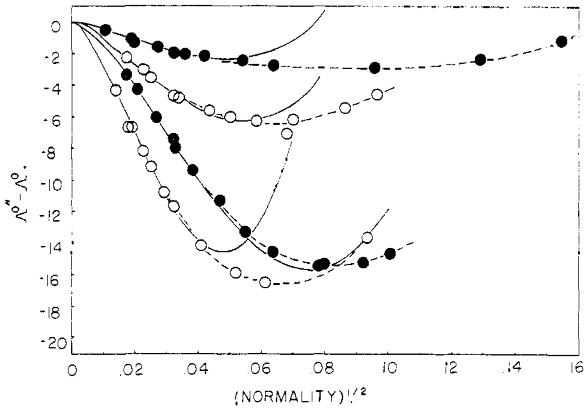

Fig. 1.—($\Lambda_0'' - \Lambda_0$) *vs.* $\sqrt{N}$, left to right: $Pt(pn)_3Cl_4$; $[N(Me)_4]_4Mo(CN)_8$; $K_4W(CN)_8$; $K_2Pt(CN)_4$. Solid lines calculated by equation 5.

There is at present no way to predict the values of $A$ and $B$ for unsymmetrical electrolytes, nor to assess the range over which equation 5 should be valid. The effects which cause the deviation of the $\Lambda^{0\prime\prime} - \Lambda^0$ curve as concentration is increased are also present at lower concentrations and hence will affect the extrapolation.

TABLE V

SUMMARY OF CALCULATIONS

| Electrolyte | $A$ | $B$ | $\Lambda^0$ |
|---|---|---|---|
| $K_4W(CN)_3$ | 4762 | 9952 | 191.2 |
| $[N(Me)_4]_4Mo(CN)_3$ | 6312 | 11440 | 157.4 |
| $Pt(pn)_3Cl_4$ | 14626 | 32301 | 164.7 |
| $K_2Pt(CN)_4$ | 2232 | 4880 | 154.6 |

Deviations from the limiting law could be due to a number of factors. Applying the treatment of

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(14) T. Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

(15) B. B. Owen, *ibid.*, **61**, 1393 (1939).

Dye and Spedding,[16] involving higher terms of the electrophoretic effect than are included in the limiting law showed that these terms are by no means negligible since about half of the total deviation could be accounted for, using reasonable values for the ion-size parameter. However, to force these terms to absorb all of the deviations would require unreasonably small values for $\mathring{a}$. This is not unexpected since the same terms are neglected in the calculation of the time-of-relaxation effect, and ion-pair formation has not been taken into account.

As an alternative approximate procedure, one can assume that the deviations are entirely due to ion-pair formation and attempt to calculate association constants using the Onsager equation for the conductance of the ionic species. The limiting conductance of the ion-pair must be estimated, and it is also necessary to estimate activity coefficients with the aid of the Debye–Hückel theory. In practice, the results for these dilute solutions are not too sensitive to the latter two approximations but are very sensitive to the form of the theoretical conductance function. Such a calculation was performed for the salts studied in this research but the association "constant" $A$ varied considerably with concentration. Typically, a ten-fold decrease in concentration from $3 \times 10^{-3}$ to $3 \times 10^{-4}$ $N$ required a 100% or greater increase in $A$ to fit the conductance data.

This once again demonstrates the inability of any single theory to cope with dilute solutions of high-charge electrolytes. One would be in a much stronger position if association constants could be measured independently; for example by the method of Cohen and Plane.[17] Unfortunately, the effect of ion-pair formation on the spectra is often too small to be useful.

Another factor which might be important is the effect of these complex ions upon the water structure. The high values for $\Lambda^0$ indicate either a small hydration tendency or an increase in fluidity of the solvent in the neighborhood of the ion due to a breakdown of hydrogen bonding. The large effect of the counter-ion on the shape of the conductance curve might be related to a cancellation of this structural effect.

It is probable that a combination of the factors mentioned is involved. If this is the case, studies involving a number of different ions of different sizes, charges and hydrophilic characteristics will be required to separate the various effects. In any event, the realm of unsymmetrical electrolyte behavior, even in dilute solutions, is not characterized by the simplicity of the univalent salts.

**Acknowledgment.**—The authors wish to thank the National Science Foundation which contributed to the support of this research at Michigan State University.

(16) J. L. Dye and F. H. Spedding, THIS JOURNAL, **76**, 888 (1954).

(17) S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957).

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

# A Study of the Electron Exchange Reaction between Tin(II) and Tin(IV) in Aqueous Sulfuric Acid Solutions

BY GILBERT GORDON AND CARL H. BRUBAKER, JR.

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The kinetics of the exchange reaction between tin(II) and tin(IV) in aqueous sulfuric acid were studied in the temperature range of 25 to 50°. Experiments were designed to determine the effects of variation in concentration of tin(II), tin(IV) $(\mathrm{SO_4^{=}})$, $(\mathrm{H^+})$ and $(\mathrm{Cl^-})$ ions. It was found that the reaction is first order with respect to tin(II) and tin(IV) and that the effect of increasing $(\mathrm{H^+})$ is to decrease the rate of exchange, and the effect of increasing $(\mathrm{SO_4^{=}})$ is to increase the rate of exchange. An empirical equation, $R/ab = 0.674\,(\mathrm{H^+})^{-2} + 0.0725\,(\mathrm{SO_4^{=}})(\mathrm{H^+})^{-1}$, which predicts the effects of $(\mathrm{H^+})$ and $(\mathrm{SO_4^{=}})$ on the rate of exchange is presented and some possible mechanisms which lead to this model are discussed. The addition of $(\mathrm{Cl^-})$ to the reaction mixture in 3.00 $M$ $\mathrm{H_2SO_4}$ increases the rate by up to a factor of 100. The rate can be calculated by the equation, $R = 4.94[\mathrm{Sn(II)}][\mathrm{Sn(IV)}][\mathrm{Cl^-}]$, above 0.5 $M$ $\mathrm{Cl^-}$, and a mechanism which leads to this model is given. Spectrophotometric examination of aqueous solutions of tin(II) in either $\mathrm{HClO_4}$ or $\mathrm{H_2SO_4}$ have been interpreted in terms of the hydrolysis of $\mathrm{Sn^{++}}$. The concentration hydrolysis constant, equal to 24.5, has been evaluated. The absorption of tin(IV) solutions and tin(II)–tin(IV) solutions in 3.00 $M$ $\mathrm{H_2SO_4}$ and tin(II)–tin(IV) solutions in $\mathrm{H_2SO_4}$ containing 1.00 $M$ $\mathrm{Cl^-}$ (3.99 $M$ $\mathrm{H^+}$) are given. The spectra have been interpreted in terms of interaction dimers containing one atom of tin(II) and one atom of tin(IV).

## Introduction

The electron exchange reaction between tin(II) and tin(IV) in hydrochloric acid has been the subject of several papers.[1,2] In both cases, the exchange reaction was found to be first order in tin(II) and tin(IV) concentrations, and an interaction dimer containing one atom of tin(II) and one atom of tin(IV) has been suggested. Our preliminary investigations indicated that the exchange was much slower in sulfuric acid than in hydrochloric acid but did proceed at a measurable rate.

We undertook the present study to try to elucidate the mechanism of the exchange reaction in sulfuric acid as part of a project in which the role of various anions as complexing agents is being studied with respect to electron transfer reactions. Our primary interest is in connection with reactions which may proceed either by direct transfer of two electrons or alternatively by the stepwise exchange of one electron at a time. We also were interested in clarification of the role of sulfate ion, in view of its effects on the tin(II)–cerium(IV) reaction.[3]

(1) C. I. Browne, R. P. Craig and N. Davidson, THIS JOURNAL, **73**, 1946 (1951).

(2) E. G. Meyer and M. Kahn, *ibid.*, **73**, 4950 (1951).

(3) C. H. Brubaker and A. J. Court, *ibid.*, **78**, 5530 (1956).