current with time occurs when species such as ferric iron or iodine are reduced in identical experiments and the results with iodate clearly show that the oxide film is indispensable for the reduction to proceed at these potentials. As soon as the oxide is removed from the electrode the iodate ion reduction current stops flowing.

Experiments with Analogous Anions.—Additional chronopotentiometric experiments have shown that the platinum oxide film produces effects entirely similar to those described above for iodate ion reduction when periodate ion is reduced, the only difference being that periodate ion in acidic solutions chemically oxidizes the platinum electrode. No effect of the oxide was detectable for the reduction of bromate or chlorate at oxidized platinum electrodes. Experiments with gold electrodes showed that the reduction of iodate ion is not noticeably different at oxidized or reduced electrodes even though oxide films are known to exist on oxidized gold electrodes.[8]

Conclusions

In a previous study[2c] it was shown that the oxidation of iodine to iodate at platinum electrodes proceeds prior to oxygen evolution at reduced electrodes but not at oxidized electrodes. Further, the potential at which the iodine is oxidized is very close to the potential at which the platinum electrode itself is oxidized. This fact and the results of the present study suggest that the kinetics of both the oxidation of iodine to iodate and the reduction of iodate to iodine at platinum electrodes involve concomitant oxidation and reduction of the platinum.

The general tendency for platinum oxide films to increase the reversibility of electrochemical couples has been cited by Kolthoff and Nightingale.[2d] However there are exceptions to this rule (*e.g.*, the oxidation of iodine to iodate)[2c], and the immediate relationship between the reduction of the oxide film and the (more reversible) reduction of the electroactive ion is not found in the other reported cases where electrode oxidation increases reversibility (*e.g.*, the ferric–ferrous couple).[2d] It seems unlikely that a single interpretation will be able to account for all of the effects on electrode reactions which the oxide films on oxidized platinum electrode have been observed to cause.

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(8) A. Hickling, *Trans. Faraday Soc.*, **42**, 518 (1946).

[CONTRIBUTION NO. 1521 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Calibration of Conductance Cells at 25° with Aqueous Solutions of Potassium Chloride[1]

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All available precision data on the conductance of aqueous solutions of potassium chloride at 25° up to concentrations of about 0.01 N were analyzed by means of the linear conductance equation $\Lambda' = \Lambda_0 + Jc$, where $\Lambda' = \Lambda + Sc^{1/2} - Ec \log c$, and $S = 94.65$ and $E = 58.74$ are theoretically predictable constants. The weighted average of the results gives $\Lambda_0 = 149.93$ and $J = 198.4$. The equation gives $\Lambda' = 151.909$ for a 0.01 *demal* solution, which agrees with the Jones and Bradshaw standard within 0.003. The equation may be used to calibrate conductance cells with potassium chloride at several concentrations up to about 0.012 N, instead of at a single fixed point.

For many years, conductance cells were calibrated according to the specifications of Kohlrausch and Holborn.[4] Kraus and Parker[5] in 1922 discovered some discrepancies in these standards, and Parker and Parker[6] shortly thereafter redetermined the absolute conductance of several potassium chloride solutions. Later, Jones and Bradshaw[7] in 1933 repeated the absolute determinations and again found discrepancies in the work of their predecessors. A repeated check by Jones and Prendergast[8] was consistent with the 1933 values to about 0.02%, but Benson and Gordon[9] summarize reasons for preferring the Jones and Bradshaw standards.

All of the recommended standards have one feature in common: absolute specific conductances are given for one fixed concentration (approximately 1.0, 0.1 and 0.01 N) for use in the nearby ranges of cell resistance. Aside from the tedium of preparing a solution precisely to a predetermined value, use of a fixed point means that a given cell must be calibrated at only one value of cell resistance. It would be preferable to determine the cell constant over a range of cell resistances, in order to be certain that no stray shunts were present. It is a matter of sad experience that a cell may behave properly at low resistances (where it is calibrated) but give increasingly unreliable results as the resistance increases. At present, no direct method is available for calibrating cells at resistances greater than that of 0.01 demal potassium chloride, but from the point of view of recent theoretical work[10] it is the range below 0.04 N in water for 1-1 salts which is most interesting. Thanks to the theory, however, it is possible to devise a method of calibrating cells at higher resistances, because it fur-

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(2) National Science Foundation Research Fellow.

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(4) F. Kohlrausch, L. Holborn and H. Diesselhorst, *Wied. Ann.*, **64**, 417 (1898); F. Kohlrausch and L. Holborn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, 1898.

(5) C. A. Kraus and H. C. Parker, THIS JOURNAL, **44**, 2422 (1922).

(6) H. C. Parker and E. W. Parker, *ibid.*, **46**, 312 (1924).

(7) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

(8) G. Jones and M. J. Prendergast, *ibid.*, **59**, 731 (1937).

(9) G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1945).

(10) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957); R. M. Fuoss, THIS JOURNAL, **80**, 3163 (1958).

nishes a method of extrapolating *linearly* from the Jones and Bradshaw 0.01 demal solution to lower concentrations.

It is the purpose of this paper to present an equation which permits the calculation of the conductance of potassium chloride solutions in water at any concentration up to about 0.012 N with an accuracy of about 0.013%. The equation is

$$\Lambda = 149.93 - 94.65c^{1/2} + 58.74c \log c + 198.4c \quad (1)$$

The coefficients of the $c^{1/2}$ and $c \log c$ terms are calculated from theory, using $D = 78.54$ and $\eta = 0.008929$ for water at 25° ($T = 298.16°$). The limiting conductance and the coefficient of the c term above are weighted averages of the best available data on the conductance of solutions of potassium chloride in water at 25°.

For 1-1 electrolytes, equation (2) has been shown[10] to reproduce conductance data for unassociated electrolytes up to concentrations corresponding to $\kappa a \backsimeq 0.2$ within a precision of 0.01%

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc \quad (2)$$

Here

$$S = \alpha\Lambda_0 + \beta$$
$$\alpha = e^2\kappa/6DkT(1 + q)c^{1/2}$$
$$\beta = \mathfrak{F}e\kappa/3\pi\eta Cc^{1/2} \times 10^{-8}$$
$$E = E_1\Lambda_0 - E_2$$
$$E_1 = 2.3026\ \kappa^2a^2b^2/24c$$
$$E_2 = 2.3026\ \kappa ab\beta/16c^{1/2}$$
$$\kappa^2 = \pi Ne^2c/125DkT$$
$$b = e^2/DkT$$

These various values[11] of the universal constants in the above equations were used: $e = 4.80223 \times 10^{-10}$ e.s.u., $k = 1.380257 \times 10^{-16}$ erg/deg., $T = 298.160 + t^0{}_c$; $\mathfrak{F} = 96493.1$ coulombs/equivalent and $C = 2.997902 \times 10^{10}$ cm./sec. The numerical constant $(1 + q) = 1.7071$. Substitution for $t = 25.000°$ gives

$$S = 159.35\ \Lambda_0/D_{25}{}^{3/2} + 4.778/\eta_{25}D_{25}{}^{1/2} \quad (3)$$

and

$$E = 2.5559 \times 10^5\Lambda_0/D_{25}{}^3 - 1122.3/\eta_{25}D_{25}{}^2 \quad (4)$$

Using $D = 78.54$ for the dielectric constant[12] and $\eta = 0.008929$ for the viscosity[13] of water at 25° and with[14] $\Lambda_0 = 149.93$, S and E have the values given in eq. 1. Uncertainty in the values of either D or η would of course affect S and E and hence J (but not Λ_0). For example, a number of values of D have been reported:[12,15,16] Wyman, 78.54; Albright, 78.48 and Malmberg and Maryott, 78.30. The corresponding values of J obtained from the data of Owen and Zeldes are 195.7, 196.2 and 199.2. The constant J of eq. 1 is fixed for a given electrolytic system; its physical significance is not pertinent to the present discussion.

Concentrations in eq. 1 are expressed in equivalents per liter, using $M = 74.557$ as the molecular weight of potassium chloride.[17] When data which were based on a different molecular weight were used, they were corrected to the standard $M = 74.557$ by the relations $\Delta c/c = -\Delta M/M$ and $\Delta\Lambda/\Lambda = \Delta M/M$. If a given set of data were based on a standard other than that of Jones and Bradshaw, they were reduced to this standard by multiplication by the appropriate factor. Now eq. 2 may be rearranged as

$$\Lambda' = \Lambda + Sc^{1/2} - Ec \log c \quad (5)$$
$$= \Lambda_0 + Jc \quad (6)$$

Equation 5 defines a new dependent variable Λ' which is the observed conductance, corrected for the known $c^{1/2}$ terms in mobility and for the known transcendental term which originates in the relaxation field. As shown by (6), Λ' is simply a linear function of concentration, a form which is of course amenable to treatment by the method of least squares.

The available data in the literature for the conductance of potassium chloride at 25° were reviewed and excluded from further consideration were those sets of data which covered too narrow a range of concentration below 0.012 N. Then the function Λ' was calculated for the remaining data. Least square lines were computed in order to obtain the best values of Λ_0 and J; then the standard deviation was calculated for each set of data, using the constants obtained from that set. Arbitrarily rejected from further consideration were all data sets whose "internal" standard deviation σ_i exceeded 0.100 Λ-unit. There remained the nine sets of data summarized in Table I. The second column gives the number of points and the third column the highest concentration used in the calculations. The values given in the fourth and sixth columns are the values of Λ_0 and J corresponding to each set of data. (It will be noted that we carried a digit in the 0.001 Λ-unit place in the calculations, in order to avoid trivial arithmetical errors in the 0.01 place, which would come in from rounding the theoretical terms $Sc^{1/2}$ and $Ec \log c$ in calculating Λ'.)

The data are arranged in the table in the sequence of increasing standard deviation. Over-all average values of Λ_0 and J were then computed, weighting each value in Table I according to the inverse *square* of the standard deviation of the set which determined it. (Several sets were given somewhat smaller weights because the points were not uniformly distributed over the working range.) The results are $\Lambda_0 = 149.93$, $J = 198.4$.

The columns headed $\Delta\Lambda_0$ and ΔJ show the deviations of the individual values of the constants from the over-all weighted averages. Values of conductance for each experimental point in each set were computed, using the final averages of Λ_0 and J; the last column of Table I gives the standard deviation σ of each set for Λ(calcd.) minus Λ(obsd.).

Finally a comparison was made at the 0.01 demal Jones and Bradshaw point, which is by definition 0.745263 g. of potassium chloride in 1000 g. of solution (both corrected to vacuum). To convert to

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[11] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, THIS JOURNAL, **74**, 2699 (1952).

[12] J. Wyman, Jr., *Phys. Rev.*, **35**, 613 (1930).

[13] J. F. Swindells, *J. Colloid Sci.*, **2**, 177 (1947).

[14] The preliminary calculations were made with $\Lambda_0 = 149.96$, which was obtained by extrapolation from a single set of the data considered. Replacing this by the final average made a negligible change in the constants S and E.

[15] P. S. Albright, THIS JOURNAL, **52**, 2098 (1937); P. S. Albright and L. Gosting, *ibid.*, **68**, 1061 (1946).

[16] C. G. Malmberg and A. A. Maryott, *J. Research Natl. Bur. Standards*, **56**, 1 (1956).

[17] E. Wichers, THIS JOURNAL, **80**, 4121 (1958).

TABLE I

SUMMARY OF CALCULATIONS

Ref.	No.	$10^4c_{\max}$	Λ_0	$\Delta\Lambda_0$	J	ΔJ	σ_i	$\Delta\Lambda'_{JB}$	σ
OZ[a]	5	92	149.96_0	0.029	195.7	−2.7	0.007	0.005	0.021
S34[b]	8	104	149.91_1	− .020	197.7	−0.7	.011	− .024	.027
BG[c]	19	100	149.89_9	− .032	203.1	4.7	.022	.018	.031
GG[d]	7	101	149.90_8	− .023	203.3	4.9	.024	.029	.030
LF[e]	8	100	149.95_7	.026	205.6	7.2	.033	.101	.059
S32[f]	20	100	149.95_9	.028	206.6	8.2	.039	.113	.062
BTU[g]	4	96	149.94_9	.018	197.7	−0.7	.059	.014	.055
D[h]	17	63	149.98_2	.051	191.8	−6.6	.041	− .012	.059
S[i]	6	100	149.86_6	− .065	223.5	25.1	.086	.189	.128

[a] B. B. Owen and H. Zeldes, *J. Chem. Phys.*, **18**, 1083 (1950). [b] T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934). [c] G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1945).[i] [d] H. E. Gunning and A. R. Gordon, *ibid.*, **10**, 126 (1942). [e] N. C. C. Li and H. Fang, THIS JOURNAL, 64, 1544 (1942). [f] T. Shedlovsky, *ibid.*, **54**, 1411 (1932). [g] R. W. Bremner, T. G. Thompson and C. L. Utterback, *ibid.*, **61**, 1219 (1939). [h] C. W. Davies, *J. Chem. Soc.*, 432 (1937). [i] V. K. Semenchenko, B. V. Erofeev and V. V. Serpinskii, *J. Gen. Chem.* (*U. S. S. R.*), **2**, 893 (1932). We are most grateful to these authors for sending us transcripts of their original data which we used in place of the published values which were interpolated to round concentrations.

moles per liter of solution, we used the equation

$$c/m = 0.99707 - 0.0272m$$

which is based on data in the International Critical Tables.[18] The equation is similar to that of Harned and Cook[19] except for the constant 0.99707 which will give c in moles/l. solution, instead of moles/1000 cc., from m in moles/1000 g. solution. At the 0.01 demal point, c = 0.0099713, Λ = 141.282 and Λ' = 151.906.

Values of Λ' at 0.01 demal were calculated for each set of data in Table I, using the constants pertinent to each set; the differences between these values and 151.906 are given in the ninth column of the table. The average of the absolute values of $\Delta\Lambda'_{JB}$ for the first four sets of data, which were given the highest weight in computing our over-all average values of Λ_0 and J on account of the low values of σ_i for these sets, is 0.019. Using the final values of the constants, we find for 0.01 demal solution

$$\Lambda' = 149.931 + 198.4\ (0.0099713) = 151.909 \quad (7)$$

which is essentially in perfect agreement with the Jones and Bradshaw value of 151.906. Therefore, considering (7) and the average $\Delta\Lambda'_{JB}$ = 0.019, and rounding to 0.01 Λ-unit, $\Lambda_0 = 149.93 \pm 0.02$. The spread in the best J-values is about 1% which would correspond to an uncertainty of 0.02 at 0.010 N; considering the agreement shown in (7), we conclude that eq. 1 may be used to calculate conductance of aqueous potassium chloride solutions in the range of the concentrations of Table I to an accuracy of 0.013%.

In practical work, a cell with constant equal to unity will give a resistance of about 700 ohms at 0.01 N and 7000 ohms at 0.001 N; this is a convenient range of resistance for precise electrical measurement. Furthermore, the solvent correction at 0.001 N for water with $\kappa_0 = 1.5 \times 10^{-6}$ is only 1%; if the latter is determined to 1% precision, the uncertainty in the solution conductance is 0.01%. At 0.01 N, the corresponding solvent correction is negligible. As already mentioned, the theoretically interesting range of concentrations for aqueous solutions (of 1-1 salts) is from zero to less than 0.04 N, which corresponds to $\kappa a \approx 0.2$ (where κ is the Debye–Hückel parameter and $a = 3 \times 10^{-8}$). The constants in eq. 1 are the weighted averages from the best available information on potassium chloride solutions. Furthermore, the equation accurately reproduces the Jones and Bradshaw fixed point. Since the form of the equation is theoretically justified, it probably can be used up to concentrations somewhat higher than the largest value of $c_{\max}$ of Table I, provided the limit κa = 0.2 is not exceeded and provided association is negligible. For potassium chloride in water, these two conditions are met if c does not exceed 0.012–0.013 N. We therefore suggest that eq. 1 be used for the calibration at 25° of cells with constants of the order of unity.

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(18) "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., p. 87.

(19) H. S. Harned and N. A. Cook, THIS JOURNAL, **59**, 1290 (1937).