A REDETERMINATION OF THE ELECTROLYTIC POTENTIALS OF SILVER AND THALLIUM.

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(*A Paper read before the Faraday Society on Tuesday, December* 15, 1908, *Dr.* T. M. LOWRY *in the Chair.*)

The potential difference between a metallic electrode and a solution containing ions of the same metal is given by the equation—

$$\varepsilon_{electrode} - \varepsilon_{electrolyte} = \text{E.P.} + \frac{\text{RT}}{n\text{F}} \log C_o$$

where C is the ionic concentration of the solution surrounding the electrode, R the gas constant, T the absolute temperature, F the charge per gram equivalent, and *n* the valency. The electrolytic potential, E.P., is defined as the potential of a metal against a normal ionic solution of the same metal. The E.P. is measured by employing the calomel or hydrogen normal electrode, and determining the E.M.F. between the electrodes of the combination, metal –solution of known ionic concentration || normal electrode. The measured E.M.F. includes the liquid potential at the junction of the two liquids, which can be calculated, in certain cases, by the Planck formula (*Wied. Ann.* **40**, 561, 1890), or as Cumming (*Zeitschr. Elektrochem.*, **13**, 17, 1907, and *Trans. Far. Soc.*, **2**, 213, 1906) has shown, it can be eliminated in some instances by employing a saturated solution of ammonium nitrate as connecting liquid. The ionic concentration can be calculated from the degree of dissociation given by conductivity or freezing-point measurements, and the value for the E.P. calculated. For room temperature 17° C. the equation becomes—

$$\text{E.P.} = \varepsilon_{electrode-electrolyte} - \frac{0.058}{n} \log_{10} C.$$

The E.P. at constant temperature is a constant for each metal, and independent of the nature of the salt employed, but depending upon the solvent. Jahn (*Zeitschr. Physik. Chem.*, **33**, 545, 1900) has shown by very exact potential measurements that the degree of dissociation of strongly dissociated electrolytes is not correctly given by conductivity determinations, but Cumming (*loc. cit.*) has shown that, in the case of silver nitrate, the degree of dissociation, calculated in the usual way from the conductivity, is a very exact measure of the dissociation between the concentrations $\frac{1}{2}$ and $\frac{1}{1000}$ normal. In the following research the electrolytic potentials of silver and thallium have been redetermined over a range of concentrations, and in different salt solutions, the ionic concentration being calculated from the conductivity, the most recent conductivity measurements being used for the purpose.

EXPERIMENTAL PART.

The E.M.F. measurements were made by the compensation method, using a Clark Fisher Potentiometer. This instrument is designed for exact E.M.F.

measurements, and has a range of 3·5 volts and reading to o·0001 volt. An Ayrton-Mather reflecting galvanometer of the d'Arsonval type was used as a detector, and the Weston cadmium cell as a standard. The cadmium cell was compared with a standard cadmium cell, standardised at the National Physical Laboratory. All measurements were made at room temperature, viz., 17° C., and are given to the nearest millivolt.

SILVER.

The silver was prepared from the chloride by fusion with sodium carbonate. The metal was then fused and cast into sticks 3–4 mm. in diameter. The sticks were cut into lengths about 20 mm. long and fused on to copper leads. The electrodes were cemented into glass tubes with marine glue, which was quite unacted upon by the liquids employed, and made water-tight joints. The electrodes were always freshly silvered before use by electrolysis of a silver potassium cyanide solution, then thoroughly washed and allowed to stand, all connected together, in a solution of the same concentration as that used in the subsequent measurements, for at least a couple of hours. Electrodes were also silvered by electrolysis of silver nitrate, and electrodes made of silver-foil and gauze were employed. Electrodes prepared as indicated showed no E.M.F. between each other when dipping into the same solution. The electrode vessels were the half elements described in Ostwald-Luther (*Hand und Hülfsbuch*, p. 377), and were connected through a vessel containing a saturated solution of ammonium nitrate to eliminate the liquid potential (Cumming, *loc. cit.*). In order to prevent the liquid surrounding the electrode from becoming impure owing to the diffusion of the saturated ammonium nitrate, a tap was interposed and measurements made through the closed tap. The calomel decinormal electrode $Hg \mid Hg_2Cl_2 \frac{N}{10} KCl \parallel$ was employed as comparison electrode. The E.M.F. of this electrode being better defined than that of the normal calomel electrode, the mercury is o·613 volt more positive than the solution (Richards, *Zeitschr. Physik. Chem.*, **24**, 37, 1897). The calomel electrode was also protected from contamination by the connecting liquid by means of a tap.

Preliminary measurements of the cell—

$$Ag \mid \frac{N}{10} AgNO_3 \parallel NH_4NO_3 \parallel \frac{N}{10} KClHg_2Cl_2 \mid Hg$$
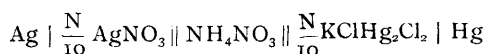
showed that the potential could be reproduced to within two millivolts, using a number of different solutions and electrodes and repeatedly resilvering the electrodes. The current flowed in the cell from the mercury to the silver. The combination gave a constant E.M.F. after standing for about an hour and remained constant for a considerable time, in most cases overnight. The following values were obtained for the E.M.F. of the combination—

$$Hg \mid Hg_2Cl_2 \frac{N}{10} KCl \parallel NH_4NO_3 \parallel \frac{N}{10} AgNO_3 \mid Ag,$$

two electrodes of silver being measured in each case ;

1.	2.	3.	4.	5.
o·4002	o·4002	o·4007	o·4018	o·4016 volts.

A rotating electrode was next measured ; for, as Kistiakowsky (*Zeitschr. Elektrochem.*, **14**, 113, 1908) has shown, different values were obtained with certain metals as electrodes when rotating electrodes were employed. The solutions were made up with recently boiled out water and care taken

to exclude air from the electrode vessel and in some cases hydrogen was passed through the solution during measurement. The results obtained were—

1.	2.	3.	4.
0·4012	0·4012	0·4010	0·4010

practically the same value as that obtained with the stationary electrodes.

Stationary electrodes were used in the subsequent measurements, at least three different cells being measured at each dilution, the three determinations agreeing to within less than 1 millivolt.

The following table shows the results obtained for silver on silver nitrate the concentrations varying from 0·1 to 0·002 gram equivalent per litre.

TABLE I.

Concentrated $AgNO_3$.	$\dfrac{\mu_0}{\mu_\infty}$.	E.M.F. of Combination in volts.	ϵ electrode solution 0·1 N.E. = + 0·613.*	ϵ electrode solution H.N.E. = O.†	0·058 log C.	E.P. (c).	E.P. (h).
0·5	0·663	0·438	+ 1·051	+ 0·774	+ 0·027	+ 1·078	+ 0·801
0·1	0·815	0·400	+ 1·013	+ 0·736	+ 0·003	+ 1·076	+ 0·799
0·2	0·900	0·364	+ 0·977	+ 0·700	+ 0·101	+ 1·078	+ 0·801
0·01	0·924	0·345	+ 0·958	+ 0·681	+ 0·118	+ 1·076	+ 0·799
0·005	0·950	0·328	+ 0·941	+ 0·664	+ 0·135	+ 1·076	+ 0·799
0·0002	0·968	0·305	+ 0·918	+ 0·641	+ 0·157	+ 1·075	+ 0·798

The degree of dissociation is calculated from the measurements of conductivity of $AgNO_3$ by Kohlrausch and Steinwehr (*Ber. kgl. preuss. Akad. der Wiss.*, **26**, 581–587; *Zeit. Elektrochem.*, **8**, 628, 1902). The mean value for the E.P. calculated from the above results is 1·076 ± 0·0005 volts, a value in good agreement with the recent determination of G. N. Lewis (*Zeit. Phys. Chem.*, **55**, 473, 1906).

A series of measurements was next made, employing silver acetate as electrolyte. The silver acetate was prepared by precipitating silver nitrate solution by a fairly concentrated solution of sodium acetate. The precipitate was three times recrystallised from hot water, and the resulting product, perfectly white and crystalline, was dried in a desiccator in the dark. The degree of dissociation was calculated from conductivity measurements, the limiting value $\mu_\infty = 89·4$ at 18° being taken from Kohlrausch and Holborn (*Leitvermögen der Elektrolyte*).

The conductivity was measured at 18° C. by the usual Kohlrausch-Ostwald method and gave the following figures—

Dilution.	Molecular Conductivity at 18° C.	$\dfrac{\mu_0}{\mu_\infty}$.
0·060	63·68	0·712
0·040	71·48	0·799
0·025	74·00	0·827
0·020	75·96	0·849
0·010	80·13	0·896
0·005	83·93	0·938
0·004	84·62	0·944
0·0025	86·00	0·962
0·0020	86·20	0·904
0·0010	87·44	0·978

* 0·1 N.E. indicates the decinormal calomel electrodes.
† H.N.E. indicates the hydrogen normal electrodes.

162   A REDETERMINATION OF THE ELECTROLYTIC

The electrodes were freshly silvered by electrolysis of silver potassium cyanide and of silver nitrate before each measurement. The E.M.F. of the combination—

$$Ag \mid \frac{N}{x} Ag\,C_2H_3O_2 \parallel NH_4NO_3 \parallel \frac{N}{10} KClHg_2Cl_2 \mid Hg,$$
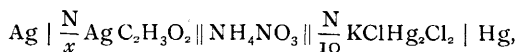
gradually increased until a constant value was reached, in about two hours, which remained constant for a considerable time, and in many cases gave the same value after standing for three days.   The following table shows the values obtained for the E.P. of silver in silver acetate solutions.

TABLE II.

Concen-trated $AgC_2H_3O_2$	$\frac{\mu_0}{\mu_\infty}$	E.M.F. of Combin-ation.	ϵ electrode $-\epsilon$ soln. 0·1 N.E. = 0·613 volt.	ϵ electrode $-\epsilon$ soln. H.N.E.=0.	0·058 log C.	E.P$_c$.	E.P$_h$.
0·060	0·712	0·382	+ 0·995	+ 0·718	+ 0·079	+ 1·074	+ 0·797
0·025	0·827	0·362	+ 0·975	+ 0·698	+ 0·090	+ 1·073	+ 0·796
0·020	0·849	0·358	+ 0·971	+ 0·694	+ 0·102	+ 1·073	+ 0·796
0·010	0·896	0·340	+ 0·953	+ 0·676	+ 0·119	+ 1·072	+ 0·795
0·004	0·944	0·323	+ 0·936	+ 0·659	+ 0·140	+ 1·076	+ 0·799
0·002	0·964	0·311	+ 0·924	+ 0·647	+ 0·157	+ 1·081	+ 0·804

The mean E.P. from all these results is + 1·075 volt ± 0·0013 volt.

Rejecting the last number, viz., + 1·081, the mean is + 1·074 ± 0·0007.

The general mean of all the measurements of the E.P. of silver, in both nitrate and acetate solutions, is + 1·0757 ± 0·0006 volt.   This value agrees with that determined by Lewis (loc. cit.), and is the most probable value for the E.P. of silver in a solution that is normal with respect to silver ions.

Abegg (Handbuch der Anorg. Chem., Band ii., abt. i., 857) refers to an unpublished research by A. Jacques and gives + 0·796 volt for the electrolytic potential of silver from measurements made in silver acetate solutions.

THALLIUM.

The thallium employed in the following experiments was the thallium puriss supplied by the Litophone Fabrikation, Triebes, and on testing was found to contain only the merest trace of impurity.   The thallium was cast into sticks 3–4 mm. in diameter, which were fused on to copper leads and then cemented into glass protecting tubes with marine glue.   The electrodes were carefully polished with fine emery-paper and then washed in water and allowed to stand, connected together in a solution of the same thallium salt which was to be used in the subsequent measurements.   The thallium nitrate, chloride, and hydroxide employed were prepared from the metal.   The nitrate was repeatedly recrystallised and the purity checked by analysis.   The chloride was prepared from the nitrate by precipitation, and after thoroughly washing was carefully dried.   The hydroxide was prepared by bubbling CO_2 free air through distilled water containing a quantity of metallic thallium in small fragments.   In this way a $\frac{1}{20}$ normal solution of thallous hydroxide could be prepared in a few hours.   The strength of the thallous hydroxide was deter-mined by titration with standard acid, employing phenolphthalein as indicator.

The first measurements of the E.M.F. of the combination—

$$Tl \mid TlNO_3\frac{N}{x} \parallel NH_4NO_3 \parallel \frac{N}{10} KClHg_2Cl_2 \mid Hg$$
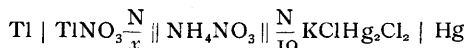
gave inconstant values, owing to the solutions becoming alkaline, by the solution of the thallium, forming thallous hydroxide, but by employing boiled-out water, and passing hydrogen through the solution during measurement, consistent values were obtained and the solutions remained neutral. The degree of dissociation of both thallium nitrate and thallium chloride was calculated from the conductivity measurements of Kohlrausch and von Steinwehr (*Ber. d. kgl. Preuss. Akad. der Wiss.*, **26**, 581–587 ; *Zeitschr. Elektrochem.*, **8**, 628, 1902), the limiting values being obtained from these results, viz., μ_∞ for $TlNO_3 = 127.75$ and μ_∞ for $TlCl = 131.47$ at $18°$ C. The degree of dissociation of thallous hydroxide was calculated from Ostwald's determinations (*Lehrbuch der Allg. Chem.*, 771).   The current flowed from thallium to mercury in the cell.   The following tables show the results obtained—

TABLE III.

Thallium in Thallous Nitrate.

Concentrated $TlNO_3$.	$\dfrac{\mu_0}{\mu_\infty}$.	E.M.F. of Combination.	$\epsilon_{Tl} - \epsilon_{soln.}$ 0.1 N.E. = 0.613 volt.	$\epsilon_{Tl} - \epsilon_{soln.}$ H.N.E. = 0.	0.058 log C.	E.P.$_c$.	E.P.$_h$.
0.10	0.78	0.724	− 0.111	− 0.388	0.065	− 0.046	− 0.323
0.02	0.84	0.753	− 0.140	− 0.417	0.100	− 0.040	− 0.317
0.01	0.93	0.775	− 0.162	− 0.439	0.118	− 0.044	− 0.321
0.005	0.95	0.788	− 0.175	− 0.452	0.134	− 0.041	− 0.318
0.004	0.96	0.793	− 0.180	− 0.457	0.140	− 0.040	− 0.317
0.002	0.97	0.813	− 0.200	− 0.477	0.157	− 0.043	− 0.320

The mean value of the E.P. from these results is − 0.042 ± 0.001 volt for 0.1 normal electrode = + 0.613 volt or − 0.319 volt for H. normal electrode = 0.   The next series of determinations were made in thallous chloride solutions, and in order to ensure that the values were constant and could be reproduced, several electrodes were used in each experiment and the solution renewed from time to time.   The following values were obtained—

TABLE IV.

Thallium in Thallous Chloride.

Concentrated TlCl.	$\dfrac{\mu_0}{\mu_\infty}$.	E.M.F. of Combination.	$\epsilon_{Tl} - \epsilon_{soln.}$ 0.1 N.E. = 0.613 volt.	$\epsilon_{Tl} - \epsilon_{soln.}$ H.N.E. = 0.	0.058 log C.	EP$_c$.	EP$_h$.
0.01	0.935	0.773	− 0.160	− 0.437	− 0.118	− 0.042	− 0.319
0.005	0.940	0.788	− 0.175	− 0.452	− 0.133	− 0.042	− 0.319
0.004	0.950	0.796	− 0.183	− 0.460	− 0.140	− 0.043	− 0.320
0.002	0.970	0.813	− 0.200	− 0.477	− 0.157	− 0.043	− 0.320

The mean value from these results is—

$$\text{E.P.}(_c) = -\ 0.042 \pm 0.0004 \text{ volt.}$$
$$\text{E.P.}(_h) = -\ 0.319 \text{ volt.}$$

An attempt to determine the E.P. of thallium was then made, using thallium hydroxide as electrolyte and using the calomel electrode saturated

164   A REDETERMINATION OF THE ELECTROLYTIC

solution of NH_4NO_3 as connecting liquid, but the values obtained for the E.P. decreased with increasing dilution of the thallous hydroxide solution. This was thought to be due to the NH_4NO_3 not eliminating the liquid potential at the junction, or, at any rate, not completely eliminating it, so an indirect method was employed, using a thallium electrode in thallous nitrate as comparison electrode and calculating the liquid potential difference by Planck's formula.

The combination—

$$\text{Tl} \mid \frac{N}{200} \text{TlNO}_3 \,\|\, \frac{N}{200} \text{TlNO}_3 \,\|\, \frac{N}{200} \text{TlOH} \mid \text{Tl}$$
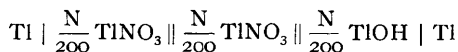
gave an E.M.F. of 0·014 volt, the current flowing from the $TlNO_3$ to the TlOH in the cell.   The liquid potential $TlNO_3 \,\|\, TlOH$ calculated from Planck's formula amounts to 0·017 volt, whence from the value for $\text{Tl} \mid \frac{N}{200} \text{TlNO}_3$ given above the E.P. can be calculated—

$$\text{E.P.} = -\,0·161 - 0·017 + 0·134 = -\,0·044 \text{ volt,}$$

a value fairly close to that obtained above and within the limit of experimental error of this indirect method.

The most probable value for the E.P. of thallium from the above measurements is − 0·0425 ± 0·0005 volt.   This agrees with that calculated from the measurements of Neumann (*Zeitschr. Physik. Chem.*, **14**, 193, 1894) and Wilsmore and Ostwald (*Ibid.*, **35**, 291, 338, 1900).

In conclusion, the author expresses his thanks to Professor Donnan and Dr. N. T. M. Wilsmore for their criticism and advice during the conduct of the above measurements.