544. *Electrochemical Studies on Polonium.*

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The potentials of the systems :

(1) Satd. calomel electrode|KCl(satd.)¦N-HNO_3¦Po^{IV} in N-HNO_3|Po on Au,
(2) Satd. calomel electrode|KCl(satd.)¦N-HCl¦Po^{IV} in N-HCl|Po on Au,
and
(3) Satd. calomel electrode|KCl(satd.)¦N-HCl¦Po^{IV}, Po^{II} in N-HCl|Pt

have been measured. The value obtained from the nitric acid system ($E_0 = +0{\cdot}76$ v) is in good agreement with that proposed by Haissinsky ($+0{\cdot}77$ v) as a mean of the results obtained from tracer experiments and it is therefore concluded that the abridged form of the Nernst electrochemical equation is valid for polonium at concentrations greater than 10^{-7}M.

HAISSINSKY[1] reported an unsuccessful attempt to measure the electrode potential of polonium directly, using 10^{-5} g. of ^{210}Po. The first indirect measurements at tracer concentrations were made by Paneth and Hevesy.[2] The rate of deposition of the polonium was measured at a series of cathode potentials, and by extrapolation of the results the " critical deposition potential " was obtained. The method was improved by Joliot,[3]

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[1] Haissinsky, *J. Chim. phys.*, 1935, **32**, 116.
[2] Paneth and Hevesy, *Sitzungsber. Akad. Wiss. Wien*, Abt. II*a*, 1913, **122**, 1037.
[3] Joliot, *J. Chim. phys.*, 1930, **27**, 119.

who made a comprehensive study of the tracer-level electrochemistry of polonium, and, later, by Haissinsky and others.[4] At very low concentrations, however, where the quantity of tracer is insufficient to cover the entire electrode surface, anomalous results have been obtained. Wertenstein,[5], Joliot,[3] and Heal [6] found no change in the deposition potential of polonium in solutions more dilute than 10^{-8}M, and it was suggested that the abridged Nernst electrochemical equation was not valid for polonium under these conditions. More precise measurements [7] showed a marked potential shift in a direction opposite to that predicted by the Nernst equation, and from the results obtained by the numerous workers on the tracer deposition of polonium, they proposed the value +0·77 v for the normal electrode potential.

Power [8] recently studied the electrochemical behaviour of polonium in 4·7M-hydrochloric acid, using a modified form of Joliot's method. Inflections were observed in the deposition–potential curve at 0·64, 0·56, 0·44, and 0·34 v, and it was concluded that these indicated several oxidation states of polonium in hydrochloric acid solution. However, the inflections are not well defined and the chemical behaviour of polonium in hydrochloric acid does not substantiate this supposition.

EXPERIMENTAL

All experimental work was carried out in a glove box in order to minimise the hazards associated with curie quantities of polonium.[9] Each determination was made on approx. 0·2 mg. (1 curie) of ^{210}Po.

System (1). The cell used for the measurements is shown in Fig. 1. To prevent contamination of the electrolyte with traces of chloride ion which would radically affect the potential, a bridge (*B*) containing nitric acid was introduced between the cell and the saturated calomel electrode. All potential measurements were made on an Electronic Instruments pH meter which had been standardised against a Pye precision vernier potentiometer.

The polonium was available as a solution in nitric acid, and spectrographic analyses revealed no impurities other than those associated with the " AnalaR " nitric acid in which it was dissolved. To ensure the purity of the polonium it was electrodeposited on to gold foil and vacuum-distilled [9] before each experiment. The metal was then dissolved in nitric acid and electroplated on to a gold wire of 0·012″ diameter which was used as the polonium electrode in the subsequent experiment. Because of the short half-life of ^{210}Po ($t_{1/2}$ = 138·4 days) a small quantity of ^{206}Pb (*ca.* 0·5%) grew into the polonium during the experiment.

On completion of the deposition the polonium electrode was washed and transferred to the cell (*A*) (Fig. 1) which contained N-nitric acid. Nitrogen was bubbled through the solution until a small quantity of the polonium had dissolved from the electrode. The nitrogen was then cut off and a reading of the potential, with respect to a saturated calomel electrode, was taken as soon as it attained equilibrium (*ca.* 10 sec.). The solution was then stirred and sampled, and the polonium concentration estimated in an air ionisation chamber.[10] A potential of 2 v was applied across the cell to prevent further dissolution of the polonium during the assaying. Under these conditions the rate of deposition of the polonium is too slow to cause a significant error in the estimation. The procedure was repeated until a series of values of the potential at various concentrations had been obtained.

System (2). In the measurements of the potential of the polonium chloride complex the procedure was the same as that described above, except that the cell and bridge were filled with hydrochloric acid.

System (3). A solution of polonium in hydrochloric acid was reduced by sulphur dioxide to the pink bivalent state in a smaller version of the cell shown in Fig. 1. Nitrogen was bubbled through the solution to remove the excess of sulphur dioxide and other gases produced by radiation decomposition. The potential of a platinum electrode in the solution, with respect to a saturated calomel electrode, was recorded as a function of time.

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[4] *E.g.*, Coche, Faraggi, Avignon, and Haissinsky, *J. Phys. Radium*, 1949, **10**, 312.
[5] Wertenstein, *Compt. rend. Soc. Sci. Varsovie*, 1917, **10**, 771.
[6] Heal, Nat. Res. Council Canada, Report M.C. 33, 1943.
[7] Haissinsky and Coche, *J.*, 1949, S 397.
[8] Power, American Report MLM 909, 1953.
[9] Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320.
[10] Cuykendall and Findlayson, American Report MDCC-341, 1946.

Results.—The results (see Table) give a mean value of E_0^{H} Po/Po(IV), N-HCl = 0·55 v, and hence K_0 for the reaction $\mathrm{Po^{4+} + 6Cl^- \rightleftharpoons PoCl_6^{2-}}$ is approximately 10^{14}.

DISCUSSION OF RESULTS

In the interpretation of the results the following factors must be taken into consideration.

Reversibility of the Electrode.—Even in dilute acid solution some spontaneous dissolution of the polonium takes place, which may be due to the effect of the intense α-bombardment on the solution in the vicinity of the electrode. Under these conditions the electrode is not in thermodynamic equilibrium with the solution. The dissolution is, however, slow (*ca.* 2×10^{-8} g./sec.) and should not appreciably affect the equilibrium potential.

α-Bombardment.—The α-flux from the electrode coated with 1 curie of polonium is of the order of 2×10^{11} α-particles per sec. per sq. cm. across the small annulus of liquid in contact with the electrode, corresponding to an energy dissipation of 31·6 milliwatts and the disruption of *ca.* 2×10^{15} solvent molecules per second. The effect of this factor on the potential is not known.

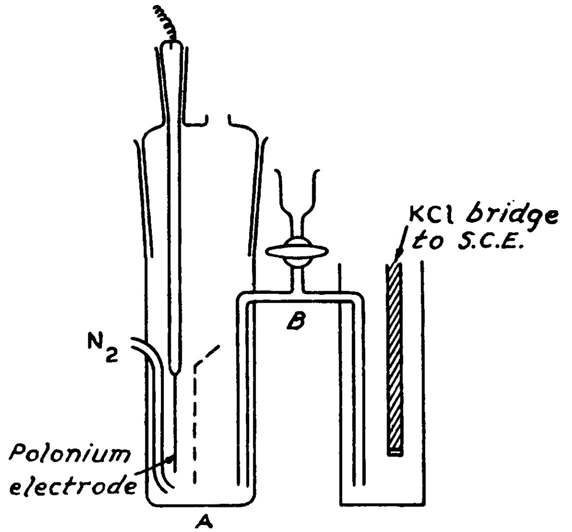

FIG. 1. *Electrolytic cell.*

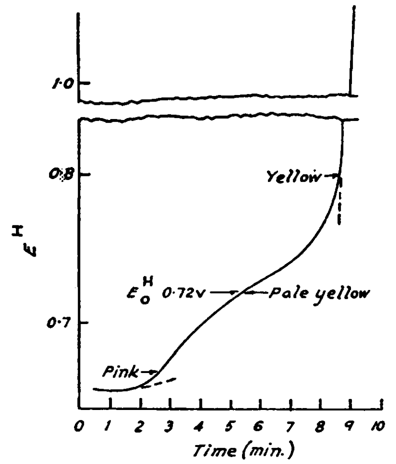

FIG. 2. *Autoxidation of polonium* : 5×10^{-4}M-Po in N-HCl.

Concentration Polarisation.—Dissolution of the polonium during the measurement of the potential will cause concentration polarisation effects in the vicinity of the electrode. This effect is reflected in the variations of E_0^{H} observed in any particular experiment and does not appear to be large. Stirring of the solution should reduce the effect, but it was found that this caused a marked negative potential drift and reproducible results could not be obtained. The magnitude of the shift was greater than would be expected from concentration effects, and its origin is not clear. Consequently all measurements were made under static conditions.

State of the Polonium in Solution.—(a) *Nitric acid solution.* It is known from transference experiments [11] and solubility determinations [12] that polonium in nitric acid is in a partially complexed state [$\mathrm{Po(NO_3)_5^-}$, $\mathrm{PoO^{++}}$, etc.]. The potential measured is that of the species of ion present in the solution, but it is probable that at least part of the polonium is present as $\mathrm{Po^{4+}}$ ions and even if this proportion were as low as 10% it would affect the reversible electrode potential by only a few millivolts. No assessment can be made of the magnitude of this factor until quantitative data are available on the state of polonium in nitric acid. The use of other acids for measurement of the potential is limited by the

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[11] Haissinsky, *J. Chim. phys.*, 1933, **29**, 453.

[12] Orban, American Report MLM 973, 1954.

tendency of polonium compounds to hydrolyse, the solubility of the polonium salts formed, and the very marked tendency to form stable complexes.

The mean value, $E_0^H = 0{\cdot}76$ v, is in good agreement with that obtained at much lower concentrations by a fundamentally different method in which the first three factors play no part, and it is in accord with the properties of polonium.[7] In particular, it lies, as would be expected, between the values for silver and tellurium in the electrochemical series.

Potential measurements.

(a) *Polonium in* N-*nitric acid.* Temperature 22°.

10^5 × Equilm. Po concn. (M)	Obs. potential (v) * (±0·001 v)	E_0^H (v) (±0·001 v)
Expt. 1. Initial quantity of polonium on electrode = 1·4 curies of ^{210}Po.		
1·31	0·447	0·763
4·07	0·450	0·758
7·27	0·452	0·757
7·59	0·453	0·756
8·77	0·454	0·756
9·85	0·454	0·756
Expt. 2. Initial quantity of polonium on electrode = 0·9 curie of ^{210}Po.		
0·37	0·442	0·766
1·07	0·447	0·764
1·41	0·447	0·764
1·56	0·447	0·762
2·62	0·449	0·761
2·89	0·450	0·760
		0·760
Expt. 3. Initial quantity of polonium on electrode = 1·7 curies of ^{210}Po.		
1·05	0·446	0·763
1·40	0·447	0·762
2·60	0·449	0·760
5·05	0·450	0·757
6·50	0·454	0·759

The results give a mean value of $E_0^H = 0{\cdot}76$ v.

(b) *Polonium in* N-*hydrochloric acid.* Temperature 22°.

10^5 × Equilm. Po concn. (M)	Obs. potential (v) * (±0·001 v)	E_0^H (±0·001 v)
Expt. 1. Initial quantity of polonium on electrode = 1·2 curies of ^{210}Po.		
0·68	0·232	0·551
1·00	0·233	0·550
1·33	0·233	0·549
2·36	0·233	0·544
2·47	0·235	0·545
2·68	0·236	0·545
3·22	0·236	0·544
4·02	0·237	0·544
Expt. 2. Initial quantity of polonium on electrode = 1·3 curies of ^{210}Po.		
0·60	0·237	0·557
0·87	0·242	0·560
1·20	0·243	0·559
2·08	0·246	0·557
2·57	0·247	0·558
3·54	0·246	0·555
Expt. 3. Initial quantity of polonium on electrode = 1·1 curies of ^{210}Po.		
0·10	0·218	0·543
0·18	0·225	0·549
0·42	0·230	0·552
0·65	0·231	0·551
1·38	0·232	0·547
1·93	0·233	0·546
2·73	0·234	0·544

* With respect to a saturated calomel electrode.

The agreement between the values obtained in this work and those obtained on the tracer scale may be evidence for the validity of the abridged Nernst electrochemical equation at dilutions greater than 10^{-7}M.

(b) *Hydrochloric acid solution.* Diffusion experiments[13] indicate that polonium in hydrochloric acid solution is present in the form of bivalent ions; there is abundant evidence[9, 14, 15] for the precipitation of hexachloropolonite from hydrochloric acid solution, and solubility measurements of polonium tetraiodide in hydriodic acid[16] indicate that the polonium is present almost entirely as the PoI_6^{2-} ion in hydriodic acid solution more concentrated than 0·02N. It therefore seems probable that the species present in hydrochloric acid solution is the $PoCl_6^{2-}$ ion, although the $PoCl_5^-$ or the $HPoCl_6^-$ ion may also be present.

Measurements of the potential of a polonium electrode in 0·1M-hydrochloric acid gave very erratic results ($E_0^H \approx 0{\cdot}63$ v). The variation in the observed values is probably due to the hydrolysis of polonium tetrachloride at this acid concentration. However, the approximate value obtained is of the correct order for a tenfold change in chloride concentration assuming the predominant ionic species to be $PoCl_5^-$ or $PoCl_6^{2-}$.

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[13] Hevesy, *Phil. Mag.*, 1914, **6**, 27.

[14] Guillot, *J. Chim. phys.*, 1931, **28**, 92.

[15] Staritzky, American Report LA 1286, 1951.

[16] Bagnall, D'Eye, and Freeman, unpublished work.

(c) *The redox potential of polonium in hydrochloric acid.* Yellow polonium tetrachloride is reduced to the pink bivalent chloride by sulphur dioxide, arsenious oxide, or hydrazine.[9] In migration experiments on a solution of polonium dichloride, the polonium was concentrated in the anode compartment of the cell and hence it is concluded that it is present in solution principally as a complex ion (*e.g.*, $\mathrm{PoCl_4^{2-}}$ or $\mathrm{PoCl_3^{-}}$). Attempts to measure the potential of the electrode system Po/Po(II) were unsuccessful. Even in the presence of reducing agent the potential of the electrode was the same as that of the system Po/Po(IV). However, in the small annulus of liquid surrounding the polonium electrode, the intense α-bombardment produces a strong oxidising effect due to the radiation decomposition of the solvent, and it seems unlikely that any of the reduced ion exists in this region. An alternative explanation is that the potentials recorded above are, in fact, those of the Po/Po(II) electrode. Although this explanation is thermodynamically feasible, it seems unlikely.

Direct measurement of the redox potential is complicated by the autoxidation of the polonium by the hydrogen peroxide and chlorine produced from the α-bombardment of the solution, and this property of the reduced polonium solution was utilised to determine the redox potential. A reduced solution of polonium dichloride was allowed to oxidise itself to the quadrivalent state and the potential of the system (with platinum, saturated calomel electrode) was plotted against time. From the curves obtained an estimate of the redox potential was made (see Fig. 2).

Consider the redox equation

$$E = E_0 + (\boldsymbol{RT}/2\boldsymbol{F}) \ln [\mathrm{Po^{4+}}]/[\mathrm{Po^{2+}}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the two equilibria $\mathrm{Po^{4+}} + n\mathrm{Cl^-} \longrightarrow \mathrm{PoCl}_n^{(n-4)-}$ ($n = 5$ or 6) and $\mathrm{Po^{2+}} + m\mathrm{Cl^-} \longrightarrow \mathrm{PoCl}_m^{(m-2)-}$ ($m = 3$ or 4). The corresponding equilibrium constants are

$$K_1 = [\mathrm{PoCl}_n^{(n-4)-}]/[\mathrm{Po^{4+}}][\mathrm{Cl^-}]^n$$

and

$$K_2 = [\mathrm{PoCl}_m^{(m-2)-}]/[\mathrm{Po^{2+}}][\mathrm{Cl^-}]^m$$

and substitution in (1) gives

$$E = E_0 + \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln \frac{K_2}{K_1} \frac{[\mathrm{Cl^-}]^m}{[\mathrm{Cl^-}]^n} \frac{[\mathrm{PoCl}_n^{(n-4)-}]}{[\mathrm{PoCl}_m^{(m-2)-}]}$$

or

$$E = E_0' + \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln [\mathrm{Cl^-}]^{m-n} + \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln \frac{[\mathrm{PoCl}_n^{(n-4)-}]}{[\mathrm{PoCl}_m^{(m-2)-}]}$$

or

$$E = E_0' - [\boldsymbol{RT}/2\boldsymbol{F}] \ln [\mathrm{Cl^-}]^{n-m} \text{ when } [\mathrm{PoCl}_n^{(n-4)-}] = [\mathrm{PoCl}_m^{(m-2)-}]$$

In principle it should be possible to determine the value of $(n - m)$ by measurements at a series of chloride concentrations. In practice, although the curves obtained were quite reproducible, the form of the graphs does not correspond exactly to the normal redox curve and E_0' cannot be estimated with sufficient accuracy to determine $(n - m)$. The deviation from normal behaviour is probably due to the fact that the system is not in thermodynamic equilibrium, although the rate of change is very slow. The system also contains small quantities of oxidising radicals, since their removal by the nitrogen stream or by the bivalent polonium is not instantaneous.

From Fig. 2, if it is assumed that the reduced and oxidised ions are $\mathrm{PoCl_4^{2-}}$ and $\mathrm{PoCl_6^{2-}}$ respectively, then E_0^{H} $\mathrm{Pt/PoCl_4^{2-}, PoCl_6^{2-}} \approx 0{\cdot}72$ v. From Luther's rule,

$$E_0^{\mathrm{H}}\ \mathrm{PoCl_4^{2-}/PoCl_6^{2-}} = [4(E_0^{\mathrm{H}}\ \mathrm{Po/PoCl_6^{2-}}) - 2(E_0^{\mathrm{H}}\ \mathrm{Po/PoCl_4^{2-}})]/(4 - 2),$$

and hence E_0^{H} $\mathrm{Po/PoCl_4^{2-}} \approx 0{\cdot}38$ v.

Most of the difficulties and uncertainties encountered in this work would be eliminated if milligram quantities of 200-yr. $^{209}\mathrm{Po}$, or even 3·8-yr. $^{208}\mathrm{Po}$, were available.

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