S 84. *New Experiments on the Cathodic Deposition of Radio-elements.*

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Deposition potentials for polonium and other metals on various cathodes in extremely dilute solution have been investigated and found to be abnormal in several instances, since they do not conform to the Nernst equation.

The normal potential of polonium is discussed, and the value ($E_h^0 = +0{\cdot}77$ v.) previously given is believed to be nearly correct.

ACCORDING to various electrochemical experiments carried out up to 1940 (Haissinsky, "Electrochimie des Radioelements," Hermann, Paris, 1946) on radio-elements on a tracer scale (*i.e.*, with quantities insufficient to cover the electrode with a complete monoatomic layer), it seemed possible to confirm the two important conclusions made on the basis of their first researches in this field by Paneth and Hevesy (*Wien. Ber.*, 1913, **122**, 1037, 1049; 1914, **123**, 1619), namely, that (1) the method of decomposition potentials of the second kind (critical potentials of deposition) being used, the Nernst electrochemical equation is valid for the variation of the critical potential with the concentration,* and (2) the deposition phenomena are defined by the potential of the electrode support and are independent of the nature of this and even of its polarity—cathode, anode, or isolated piece.

It is obvious that the second point is a consequence of the first, which supposes the fulfilment of some other conditions, namely, that (1) the deposition potential corresponds to a primary process (this is probably not true for polonium deposition in basic solution), (2) the deposition is not accompanied by overvoltage phenomena, and (3) the radio-element does not possess specific affinity for the support, which would lead to an under-voltage (deposition of polonium on platinum seems not to satisfy this condition).

A close examination (Haissinsky, *J. Chim. physique*, 1946, **43**, 66) of the theoretical aspect of this whole question brings us, however, to some difficulties, namely, that for deposits of less than a monoatomic layer, the forces acting between the support and the deposited atoms must intervene and vary from one metal to another. It has been shown that the experimental observations can be explained by taking into consideration the heterogeneity of metallic surfaces conditioned by the existence of "active centres." But this interpretation enabled us to conclude that the independence of the critical potential of the nature of the electrode and, consequently, the validity of the Nernst equation lose their generality in the region of very dilute solutions. It was predicted that other cases than that of polonium on platinum might be found where the deposition potential would be "abnormal."

Now, the validity of the Nernst equation has already been contested on the basis of the experiments by Mrs. Wertenstein (*Compt. rend. Soc. Sci. Varsovie*, 1917, **10**, 771) and of Joliot (*J. Chim. physique*, 1930, **27**, 119). They did not observe measurable variation of the deposition potential of polonium when its concentration varied in the ratio 100 : 1 (between about 10^{-8} and 10^{-10} N.). On the other hand, systematic measurements of the cathodic deposition of bismuth on gold and silver between 10^{-6} and 7×10^{-12} N, using radium-*E* and thorium-*C* as tracers, have clearly shown the validity of the law in this case (Haissinsky, *ibid.*, 1935, **32**, 116). Measurements of the deposition potential of technetium in 10^{-12} N-solution, carried out by Flagg and Bleidner (*J. Chem. Physics*, 1945, **13**, 269), also gave, by means of the Nernst equation, a value for the normal potential of the electrode $Tc|TcO_4^-$ which is well within the potentials of the homologous electrodes of manganese and rhenium. The non-variation of the polonium potential could then be explained by the high valency (IV) of the element and the poorness of the accuracy of the measurements.

In order to elucidate this problem and verify the theoretical conclusions mentioned above, we have, since 1945, undertaken a systematic study of the influence of the various factors concerned, especially the nature of the electrode and the concentration, on the kinetics and the equilibrium conditions. We have chosen lead and bismuth, with thorium-*B* and -*C* as indicators, in order eventually to extend the measurements to the scale of weighable quantities. Furthermore, the normal potentials of these two metals are well known.

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* The validity of the Nernst equation in this case does not necessarily signify that if, *e.g.*, a silver plate is immersed in a 10^{-10} N-silver nitrate solution, the potential of the metal would be that predicted by this equation. The Hevesy and Paneth method is somewhat related to the potential determination by polarographic techniques but is much more sensitive and highly specific. For details see Haissinsky (*op. cit.*).

In the meantime, Heal in 1946 (Natl. Res. Council, Montreal Lab. Report, MC 33) stated that the critical potential of polonium in 10^{-13} N- remains the same as in 10^{-8} N-solution. This variation of concentration corresponds to a potential variation of 0·057 × 5/4 = 0·07 v., which exceeds the error of measurement. Finally, according to Haenny and Mivelaz (*Helv. Chim. Acta*, 1948, **31**, 633), the deposition potential of radio-zinc in 10^{-15} N-solution gives a deviation from the Nernst equation of about −0·18 v.

Heal's conclusion did not seem convincing, since his potential curves have no inflexion point permitting the determination of a critical value. As to the results on radio-zinc, it could be objected that a possible contamination of some 10^{-12} g./c.c. of ordinary zinc would be sufficient to explain the observed discrepancy.

We decided nevertheless to extend our experiments on polonium in order to verify Heal's conclusion under proved conditions.* The main results we have obtained are as follows.

(1) *Lead.* The critical potentials of $0·6 \times 10^{-10}$ N-thorium-*B* in 0·1N-acetic acid solution (chosen in order to reduce anodic formation of the dioxide) on gold, silver, copper, and bismuth are respectively −0·66, −0·655, −0·665, and −0·675 v., saturated calomel being the reference electrode. These values are in very good agreement with the potential, −0·67 v., calculated from the Nernst equation. On nickel, the results are less reproducible, but one can clearly see from the curve that, there too, the critical potential is close to the theoretical value. On the other hand, on tantalum the critical potential is close to −0·85 v. and corresponds to an overvoltage of 0·18 v. Measurable quantities are deposited at lower potentials. It seems that this is quite a general phenomenon; in systems having abnormal deposition potentials, the results are not very reproducible and some deposition is observed below the deposition potential—the deposited quantities are either independent of, or slowly increasing with, potential. This is also the case for the deposition of platinum. In solutions between 10^{-6} and $0·6 \times 10^{-10}$ N. the critical potential is practically the same (~ −0·53 v.) and is close to the theoretical value (−0·55 v.) for the most concentrated, but corresponds to an undervoltage in the more dilute, solutions. This behaviour is quite different in solutions containing weighable quantities of lead (10^{-2} to 10^{-5} N.), where an overvoltage increasing with the dilution is observed. The transition between the two opposite effects is situated in the region of the formation of a monoatomic layer.

(2) *Bismuth.* The previous measurements on bismuth isotopes (Haissinsky, *loc. cit.*, 1946) have been completed by the determination of the critical potential on gold in 10^{-13} N-solution (in N-nitric acid). The value found is −0·26 v. (referred to the saturated calomel electrode), in good accordance with that calculated from the Nernst equation (−0·277 v.). On platinum, the deposition is accompanied by an undervoltage; a sudden increase of the deposition velocity is observed at −0·10 v., but some thorium-*C* is deposited even at more positive potentials. On tantalum the deposition is carried out with an overvoltage of some centivolts.

(3) Also in the case of polonium on tantalum in 10^{-9} N-solution (in 0·3N-nitric acid), there is a considerable overvoltage, relative to the deposition of gold, of 0·18 v., and the reproducibility of the results is poor. On tungsten the overvoltage is 0·14 v. On molybdenum, the polonium is deposited in appreciable quantities at all potentials examined, *i.e.*, between +0·30 and −0·05 v., with a minimum of deposition at about +0·15 v.

The experiments carried out in 10^{-13}N-solution differed from those of Heal as follows. (*a*) We have measured the deposited quantity at each potential after a time (between 8 and 12 hours instead of 1 hour as in Heal's experiments) sufficiently long for us to be sure that the equilibrium distribution between the electrode and the solution was attained. (*b*) The deposition was measured with a proportional amplifier. (*c*) We kept the solutions sufficiently acid (1·5N-nitric acid) to avoid completely any formation of colloidal polonium. It is known that for 10^{-9}N-solutions, the acidity has no effect on the cathodic critical potential of polonium (Schneidt, *Wien. Ber.*, 1929, **138**, 755).

In spite of these and other precautions, the fluctuations in the amounts deposited on gold cathodes are important, and it seems that here the results are much more sensitive to the experimental conditions than in more concentrated solutions. In particular, the origin and the " history " of the gold foil, and probably also the acidity, here have a notable effect on the quantities deposited. Our experiments nevertheless show clearly that the variation of the critical potential is not only not given by the Nernst equation but is in the opposite sense. With a set of gold electrodes of the same origin and previously submitted to nearly the

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* The experiments on lead and bismuth isotopes have been carried out by A. Coche, as part of a thesis to be submitted for the degree of Docteur ès Sciences; those on polonium in 10^{-13}N-solutions are in collaboration with Mrs. Faraggi and P. Avignon.

same treatment, we have obtained a critical potential of $+0{\cdot}53$ v., as compared with $+0{\cdot}39$ v. observed in 10^{-9} N-solution. The effect is less marked on silver, in 0·75N-nitric acid solution, the value found being $+0{\cdot}45$ v.

Thus, the experiments on various radio-elements show that the nature of the electrode can strongly influence the deposition phenomena. On tantalum, the deposition is characterised in the three cases studied by a more or less important overvoltage caused perhaps by the passivity of the metal. This is probably also the case with tungsten. On platinum, the deposition is, in all the cases examined, accompanied by an undervoltage, whose value varies with the conditions. Even on a metal such as gold, which has generally a normal behaviour, the deposition of polonium in extremely dilute solution is associated with an appreciable undervoltage. As the deposited amounts are here of the order of 10^{-7} of a monoatomic layer, it seems legitimate to think that this is due to the attractive action of some very rare spots, " active centres," of the surface. The sensitivity to exterior conditions and the diminution of the effect with the increase of the concentration are thus explained.

The relationships between the deposition potential and the surface structure are probably neither direct nor simple and require further research, but the intervention of this structure in the deposition phenomena is also demonstrated by the following experiments.

The electrodes with the polonium deposit were applied, after the electrolysis, to Ilford Nuclear Research plates (type C2). After development, microscopical examination enabled us to establish the distribution of the polonium atoms on the surface and the distribution of the α-ranges.

When the electrolysis was carried out on gold in 10 c.c. of solution containing 1·5 e.s.u. of polonium ($\sim 10^{-10}$N.) in order to obtain a deposit of 0·06 e.s.u./cm.^{2}, the range distribution gave a very well-defined peak corresponding to 21·5 μ. (in the Ilford emulsion), which is just the normal α-range for polonium according to our calibration. An appreciable number of tracks, however, were found which possessed ranges inferior to the normal value: 2·6% of 14·5 μ., 1% of 9·4 μ., etc.

If the deposit in the same solution is stopped at an intensity of 4×10^{-5} e.s.u./cm.^{2}, the distribution is considerably changed; the peak is broader and corresponds to 19·5 μ. and the number of shortened tracks is much greater. In much more dilute solutions the deformation, for the same amount deposited, is more strongly accentuated, the maximum range and the distribution varying with the origin and the " history " of the metal. Thus in 10^{-13} or 10^{-14} N-solutions the statistics give peaks varying between 7·5 and 18·8 μ.

For deposits on silver prepared under similar conditions, we have observed a nearly normal distribution. On platinum and nickel, the distribution is intermediate between that on gold and that on silver.

The traces of nearly the same length tend to be grouped together on the various parts of the surface. Furthermore, in the more concentrated solutions (5×10^{-12} to 10^{-10} N.) we frequently observed " stars " which correspond to aggregates containing thousands of polonium atoms, and whose centres often seem to be situated at a certain depth inside the electrode. The possibility of the stars being of radio-colloidal origin is excluded, as our solutions were strongly acid.

The shortening of the α-ranges, limited to a very small number of polonium atoms, clearly indicates that these penetrate partly in the weakest, most " infirm " points of the surface: these can be identified with the postulated active centres. The deposition of radio-elements in very dilute solution thus gives us a method for the study of the micro- and ultramicro-structure of metallic surfaces, as has already been suggested (Haissinsky, Faraday Society Discussion on Electrode Processes, 1947, p. 192). The bearing of the results on research in nuclear physics will be discussed elsewhere (Coche, Faraggi, Avignon, and Haissinsky, *J. Physique*, in preparation).

From the point of view of theoretical electrochemistry the behaviour of metallic ions in the electrolysis of very dilute solutions is now more satisfactory than it previously seemed to be. We see, however, that it is dangerous to use the critical potentials measured in these solutions for the calculation of an unknown normal potential. Such an extrapolation should be made only if the potential varies with the concentration and if it is independent of the nature of the electrode, at least for several metals. For this reason, the normal potential of polonium ($E_h^{\circ} = +0{\cdot}77$ v.) given by Paneth and Hevesy and recalculated by one of us has no longer a sufficient experimental basis. We think, nevertheless, that this value is not very far from the true one and that the position assigned to this element in the table of the normal potentials, between tellurium and silver, is fairly correct, for the following reasons. (1) The potential measured in 10^{-9} N-solution, which was used for the extrapolation, is the same on gold and silver, and the deposition velocities on other, less noble metals, agree with those given by the potential curve. (2) It is fairly reproducible and is independent of the origin and the previous treatment of the metal, as well as of the acidity, within large limits. (3) It is sharply defined, the amounts deposited below this potential being negligible. (4) An equilibrium distribution which can be obtained either by deposition or by dissolution corresponds to each potential, *i.e.*, the deposition process is a reversible one (Haissinsky, *J. Chim. physique*, 1933, **30**, 27). (5) The behaviour of polonium salts towards various reducing agents is, compared with that of other metals, in agreement with the position between tellurium and silver (Guillot and Haissinsky, *Bull. Soc. chim.*, 1935, **2**, 239). (6) Finally, the extrapolation from the potentials of the neighbours of polonium in the periodic system is not inconsistent with the above conclusion.

One can understand from the recent paper of Johnson, Leininger, and Segre (*J. Chem. Physics*, 1949, **17**, 1) that the arguments (3), (4), and (6) are also valid for the cathodic potential of astatine on gold. The value found by these authors in 10^{-13} N. solution is $+1{\cdot}22$ v., referred to the hydrogen electrode. Here an additional uncertainty is involved since the valency of the positive ions is not known. It seems, in any case, that astatine is not only the most noble metalloid, but also one of the most noble metals.

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