CCCLXXXV.—*Studies of Electrolytic Polarisation. Part IV. The Electro-deposition Potentials of Iron, Cobalt, and Nickel.*

By Samuel Glasstone.

It is well known that, in order to cause the electro-deposition of the metals of the iron group from aqueous solutions of even their simple salts, it is necessary to apply a cathodic potential which is considerably more negative than the theoretically reversible potential in the same solution; there is thus an "overvoltage" or retardation of metallic deposition. In every case, owing to the low overvoltage of hydrogen at these metal surfaces, the evolution of this gas accompanies the electro-deposition of the metal, and consequently hydrogen gas or hydrogen ions have been commonly regarded as the chief factor retarding the deposition of metal. In general, we may say that the deposition of a bivalent metal at the cathode involves the process

$$\underset{\text{(Ions in soln.)}}{M^{\cdot\cdot} + 2\ominus} \longrightarrow \underset{\text{(Atoms deposited.)}}{M} .$$

If this process occurs rapidly there will be no accumulation of ions in the vicinity of the cathode and the metal will be deposited at its normal reversible potential; on the other hand, if this process is retarded, deposition will not occur at this potential and the electrode will become polarised. When the potential is made more negative, the increased electron concentration will enable the above process to take place sufficiently rapidly for metallic atoms to be deposited. According to Foerster (*Z. Elektrochem.*, 1916, **22**, 85), hydrogen gas acts as a negative catalyst for the above process in the case of iron, cobalt, and nickel, and consequently the simultaneous deposition of hydrogen retards the deposition of metal. It should be pointed out that the deposition process which was considered to be retarded is a heterogeneous one, since the ions are in solution and the atoms are deposited on the solid electrode; Smits ("The Theory of Allotropy," 1922, pp. 132, 334; *Trans. Faraday Soc.*, 1924, **19**, 772), however, considers that heterogeneous equilibrium is always reached rapidly and that ions and electrons are deposited on the cathode as fast as they are brought up to it. The combination between ions and electrons is then supposed to occur in the solid electrode and is consequently a homogeneous process; if this process does not occur rapidly, then ions and electrons will accumulate until an increased negative potential results in a greater electron concentration and a consequent removal of ions to form undissociated atoms. Smits considers that hydrogen gas is a negative catalyst for this process which occurs in the solid electrode. Kohlschütter (see *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 229, for summary), on the other hand, attributes an entirely different rôle to the hydrogen which is liberated with the metal; a film of compressed gas is said to be present at the cathode, and it is considered that metallic atoms are deposited in this medium, which has considerable viscosity. The film of hydrogen behaves like an adsorption film of colloid in metal deposition and prevents the aggregation of small, metallic crystals. The metal is thus deposited in a highly dispersed form with a high free energy, and therefore an excess negative potential is required for its deposition; this form of metal, however, is in a state of strain and so there will be some tendency, opposed by the gas film, for it to change into a more stable form and thus give rise to the well-known contraction and peeling effects observed in the deposition of the iron-group metals. Kohlschütter (*loc. cit.*) deduces that with decreasing hydrogen-ion concentration of the electrolyte the polarisation should first increase, pass through a maximum, and then decrease; the argument is, however, open to objection. It is considered, too, that the contraction of the metallic deposit should vary in the same manner with varying hydrogen-ion concentration of the electrolyte; but Alvierti (*Atti R. Accad. Lincei*, 1920, **29**, 453) states that the contraction of a nickel deposit is decreased by simultaneous evolution of hydrogen in proportion to the amount evolved, and this will obviously be greater in solutions of greater hydrogen-ion concentration. Frölich and Clark (*Z. Elektrochem.*, 1925, **31**, 649) have shown that there is a similarity between the overvoltage of metal deposition and the hydrogen overvoltage at the cathodes of these metals; for example, iron, cobalt, and nickel have large metal deposition overvoltages but small hydrogen overvoltages, but with mercury and lead the conditions are reversed. Adopting the "hydride" theory, these authors attribute the overvoltage of metal deposition to the formation of stable hydrides in the case of the low-overvoltage metals; the deposition of metal does not occur until the hydride has accumulated to a sufficient extent to decompose rapidly and so polarisation results. Le Blanc (*Trans. Faraday Soc.*, 1914, **9**, 251) has put forward a theory in which hydrogen appears to play no part; it is considered that the dehydration of the ions in solution must occur before the unhydrated ions can take up electrons and then be deposited. If the dehydration process occurs slowly, polarisation will result and a higher cathodic potential will be required in order to cause deposition of metal; this would be similar to the polarisation which is observed in the electrolysis of cuprocyanide solutions owing to the slowness of the process $Cu(CN)_2' \longrightarrow Cu^{\cdot} + 2CN'$ (Le Blanc and Schick, *Z. physikal. Chem.*, 1903, **46**, 213). It is doubtful whether hydrogen gas could influence the speed of the dehydration, although it is possible that certain ions, competing with the metallic ion for water molecules, might influence the degree of hydration and the rate of dehydration. This theory was accepted by Newbery (J., 1917, **111**, 470), and Isgarishev and Berkmann (*Z. Elektrochem.*, 1922, **28**, 40) consider that they have obtained evidence in favour of the dehydration hypothesis.

An examination of these theories shows that it is essential to know exactly how the overvoltage of metal deposition varies with the hydrogen-ion concentration of the electrolyte; some work in this connexion has been done by Schweitzer (*ibid.*, 1909, **15**, 602) and by Schildbach (*ibid.*, 1910, **16**, 967), but the summary given by Foerster (*loc. cit.*) shows the difficulty of interpreting the results. It appeared to the present author that the use of a series of buffer solutions of known hydrogen-ion concentrations and the application of his extrapolation method for measuring the potentials of polarised electrodes (J., 1924, **125**, 250, 2414) might throw further light on the subject of the electro-deposition of the iron-group metals.

EXPERIMENTAL.

Electrolytic Solutions.—The requisite amount of nickel, iron, or cobalt salt was added to a buffer solution—usually one of Walpole's (J., 1914, **105**, 2501)—and the hydrogen-ion concentration of the solution roughly determined by means of indicators. In some cases potassium sulphate was added in order to increase the conductance of the solutions.

Electrodes.—The cathodes were sheets of copper foil, generally of about 7·5 sq. cm. exposed area, on which the metal under investigation was deposited by electrolysis; the anode consisted always of a short piece of platinum wire. Whenever iron or chloride solutions were being electrolysed, or when it was desired to exclude oxygen from the solution, the cathode was placed inside a porous pot and the anode in the surrounding liquid.

Materials.—The ferrous sulphate was of A.R. quality and the nickel and cobalt sulphates were good commercial specimens supplied by the British Drug Houses, Ltd. Some experiments were made with a special sample of nickel sulphate which was free from iron and cobalt, but the results did not appear to differ from those given by the less pure material. The other salts used were the purest obtainable commercially, and, where possible, of A.R. quality.

Measurement of Potential.—The current passing between the electrodes was increased by stages and was held constant for 1 minute before the potential of the electrode was measured by the commutator-extrapolation method, using the commutator described in previous work (J., 1923, **123**, 2926). The reference electrode was in every case a calomel electrode in a saturated solution of potassium chloride; no allowance was made for diffusion potential.

Deposition of Nickel.—Table I gives the cathodic potentials, on the H_2(1 atm.)|N-H$^{\bullet}$ = 0 scale, of a nickel electrode at various *C.D.*'s in various acetate buffer solutions containing *N*-nickel sulphate; in one case, a *N*/50-sulphuric acid solution was used instead of a buffer mixture. All experiments in this series were carried out at room temperature (roughly 15°).

TABLE I.

C.D. (amps. × 10^{-4}/cm.^{2}).	Cathode potentials in *N*-$NiSO_4$.				
	N/50-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.	p_H 6·0.
0·14	−0·14	−0·18	−0·21	−0·25	−0·26
0·28	−0·18	−0·22	−0·24	−0·30	−0·31
0·42	−0·21	−0·29	−0·28	−0·35	−0·39
0·56	−0·24	−0·34	−0·34	−0·39	−0·45
0·84	−0·30	−0·40	−0·39	−0·46	−0·50
1·40	−0·37	−0·45	−0·45	−0·54	−0·57
2·80	−0·43	−0·51	−0·52	−0·58	−0·58
4·20	−0·47	−0·57	−0·57	−0·60	−0·60
5·60	−0·52	−0·58	−0·59	−0·61	−0·62
8·40	−0·57	−0·59	−0·60	−0·62	−0·64
12·0	−0·59	−0·61	−0·61	−0·63	−0·66
20·0	−0·60	−0·62	−0·62	−0·64	
40·0	−0·61	−0·64	−0·64	−0·65	
80·0	−0·62	−0·65	−0·65	−0·66	

For purposes of comparison, the cathodic potential of a polarised nickel electrode in the acetate buffer solutions of p_H 5·0 and 6·0 alone (*i.e.*, no nickel salt being present) at various *C.D.*'s is given in Table II.

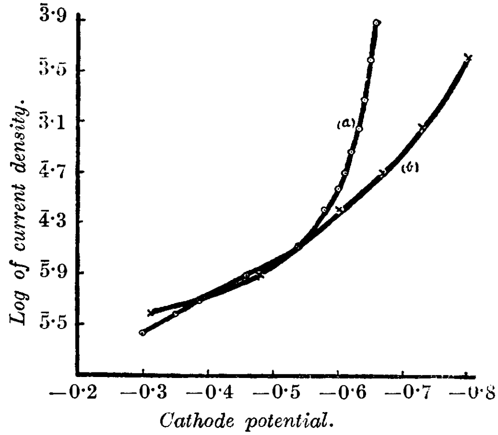
TABLE II.

Cathode Potentials.

C.D. (amps. × 10^{-4}/cm.^{2})	0·28	0·56	0·84	1·40
p_H 5·0	−0·19	−0·39	−0·48	−0·54
p_H 6·0	−0·36	−0·44	−0·54	−0·72
C.D. (amps. × 10^{-4}/cm.^{2})	2·80	5·60	12·0	40·0
p_H 5·0	−0·60	−0·67	−0·73	−0·80
p_H 6·0	−0·83	−0·92	−0·97	−1·00

An examination of Table I shows that in each case the cathode potential rises fairly rapidly, with increasing *C.D.*, until a value of − 0·57 volt is reached, after which it only changes very slightly. By comparing the results given in Tables I and II and also the log *C.D.*-potential curves in Fig. 1 for a solution of p_H 5·0, (*a*) containing *N*-nickel sulphate and (*b*) in the absence of nickel salt, it is seen that there is a distinct break at the potential of − 0·57 volt in the solutions containing nickel sulphate, and sometimes a slight break at the potential at which hydrogen is first evolved * (− 0·41 volt in solution of p_H 5·0). The difference in the two curves (Fig. 1) can only be due to the presence of nickel ions in one of the solutions, and it was always observed that nickel was deposited on the cathode when the potential exceeded that at the break-point. It seems probable, therefore, that the break at the potential of − 0·57 volt is due to the commencement of the deposition of nickel at 15°; this initial deposition potential is independent of the hydrogen-ion concentration of the electrolytic solution. By using a polished

FIG. 1.



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* The minimum (or bubble) overvoltage of hydrogen at a nickel cathode was 0·12 volt (approx.) in all the solutions examined, at room temperature.

copper cathode, the lowest *C.D.* at which nickel was deposited from any solution could be readily determined by observation of the electrode surface after being used for a short time at each of a number of gradually increasing *C.D.*'s; the potential at the lowest *C.D.* necessary for nickel deposition was always very near to — 0·57 volt. It is possible that this potential may have been affected by the formation of a nickel–copper alloy, but the coincidence of the minimum potential for metal deposition with the breaks in the *C.D.*–potential curves suggests very strongly that nickel commences to be deposited from a *N*-solution of its sulphate at a potential of — 0·57 volt at 15°, independently of the hydrogen-ion concentration. It will be observed that, as the hydrogen-ion concentration of the solution increases, the *C.D.* at which nickel deposition commences becomes higher; this is to be expected, since, with increasing concentrations of hydrogen ions, a larger current can be carried by these ions without having recourse to the nickel ions. It is quite clear that the practice hitherto adopted of comparing the cathode potentials in different solutions at the same *C.D.* (see, *e.g.*, Foerster, *loc. cit.*) may not indicate the general behaviour of the electrode in these solutions; the only satisfactory method of comparison, as in the investigation of hydrogen evolution (Glasstone, J., 1924, **125**, 2414), is to consider the potentials at which a new process—in this case deposition of metal—is just commencing. The trustworthiness of the above results for the minimum deposition potential of nickel has been confirmed by the following experiments with other solutions.

In order to determine the effect; if any, of anions on the deposition potential of nickel, a number of electrolytic solutions were used which contained only one anion in addition to the hydroxyl ion; in one case, nickel acetate was dissolved in the acetate buffer solution, whilst other solutions consisted of nickel sulphate only, nickel sulphate in *N*/10-sulphuric acid, nickel chloride in *N*/50-hydrochloric acid, nickel nitrate in *N*/50-nitric acid, saturated nickel ammonium sulphate, and saturated nickel potassium sulphate. Other solutions were the same as those used in the first part of this work, with the addition of ammonium persulphate, hydrogen peroxide, or gelatin. In every case, deposition of nickel commenced at a potential of — 0·57 volt at 15° from a *N*-solution of a nickel salt. The *C.D.* at which deposition commenced varied somewhat in the different solutions and was much higher in those containing oxidising agents, but the potential was always constant within 0·01 volt. The use of a wire cathode did not affect the results (compare Küster, *Z. Elektrochem.*, 1901, **7**, 688), neither did the complete elimination of gaseous oxygen by working in an atmosphere of hydrogen. By altering the concentration of nickel salt in the solution to *N*/100, the deposition potential became 0·06 volt more negative; this agrees with the change in the concentration of bivalent nickel ions.

A series of experiments was performed at 95°, using the same nickel sulphate and acetate buffer solutions; the results are given in Table III. The p_H values are only approximate owing to the change in temperature. The cathode potentials of a nickel electrode in an acetate buffer solution only, of p_H 6, are given in col. 6 for purposes of comparison.

TABLE III.

C.D. (amps. × 10^{-4}/cm.^{2}).	Cathode potentials in *N*-$NiSO_4$ at 95°.				
	p_H 2·8.	p_H 4.	p_H 5.	p_H 6.	p_H 6 (no Ni).
2·8	−0·16	−0·19	−0·23	−0·28	−0·25
4·2	−0·17	−0·21	−0·24	−0·29	−0·29
5·6	−0·18	−0·23	−0·25	−0·30	−0·31
8·4	−0·21	−0·26	−0·26	−0·30	−0·34
12·0	−0·23	−0·28	−0·27	−0·30	−0·37
20·0	−0·26	−0·29	−0·29	−0·30	−0·41
40·0	−0·29	−0·30	−0·30	−0·31	−0·44
80·0	−0·30	−0·31	−0·31	−0·31	−0·45
160·0	−0·31	−0·31	−0·31	−0·31	−0·47

These results indicate that the change in direction of the *C.D.*-potential curves for nickel solutions occurs at about − 0·29 volt; this may be regarded as the deposition potential of nickel from a *N*-solution of its simple salts at a temperature of 95°. Observations with a polished copper cathode have established the fact that no nickel is deposited at this temperature until the potential reaches − 0·29 volt. Experiments with solutions of nickel chloride and acetate led to the same conclusion.

Measurements have also been made at 55°, at which temperature nickel commences to be deposited at a potential of − 0·43 volt; this value is independent of the hydrogen-ion concentration of the solution. Table IV summarises the results for different temperatures.

TABLE IV.

Deposition potential of nickel from *N*-solutions.

Temperature	15°	55°	95°
Potential	−0·57	−0·43	−0·29
Overvoltage	0·33	0·19	0·05

The overvoltage values have been obtained by taking − 0·24 volt as the reversible potential of the Ni|*N*-$NiSO_4$ electrode (*Abh. Deut. Bunsengesellschaft*, No. 5, 1911), and neglecting its small temperature coefficient. The temperature coefficient of overvoltage of nickel deposition is thus − 0·0035 volt/degree over the range investigated.

Deposition of Iron.—Table V contains the results of a series of measurements with *N*-ferrous sulphate in acetate buffer solutions of varying p_H, and in one case in *N*/50-sulphuric acid, at 15°.

TABLE V.

Cathode potentials in *N*-$FeSO_4$.

C.D. (amps. × 10^{-4}/cm.^{2}).	*N*/50-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.
0·14	−0·46	−0·47	−0·47	−0·47
4·2	−0·46	−0·49	−0·49	−0·53
8·4	−0·46	−0·52	−0·50	−0·58
20·0	−0·48	−0·57	−0·56	−0·60
40·0	−0·53	−0·68	−0·68	−0·68
80·0	−0·68	−0·70	−0·69	−0·70
160·0	−0·70	−0·71	−0·71	−0·71

These results show that in every case the cathode potential increases at first slowly, then jumps to the value — 0·68 volt, after which the increase, with increasing *C.D.*, is comparatively slow. This potential, at which the *C.D.*-potential curve changes its direction, has been found, by observations with a polished copper cathode, to be that at which electro-deposition of iron commences from a *N*-solution of its simple salts. Experiments have been made with ferrous ammonium sulphate solutions, both in the presence and the absence of free sulphuric acid, and with ferrous chloride in *N*/50-hydrochloric acid and in acetate buffer solutions; in every case, the deposition potential of iron at 15° is — 0·68 ± 0·01 volt.

Measurements of the initial deposition potential of iron have also been made at other temperatures and the results are summarised in Table VI.

TABLE VI.

Deposition potential of iron from *N*-solutions.

Temperature	15°	36°	55°	70°	90°
Potential	−0·68	−0·55	−0·49	−0·46	−0·46
Overvoltage	0·22	0·09	0·03	Nil.	Nil.

The reversible potential of iron in a *N*-solution of a simple ferrous salt is probably — 0·46 volt (Hampton, *J. Physical Chem.*, 1926, **30**, 980), and so it appears that at temperatures above about 70° iron may be deposited almost reversibly.

Deposition of Cobalt.—Measurements with *N*-solutions of cobalt salts have been made as with nickel and iron; the results are summarised in Tables VII and VIII. In each case, independently of the hydrogen-ion concentration, there is a break in the variation of potential with *C.D.* at — 0·56 volt; this is the potential at which deposition of cobalt commences. Experiments with cobalt chloride in hydrochloric acid solution, with the nitrate in nitric acid, and with the acetate in acetate buffer solutions all gave a similar result.

TABLE VII.

C.D. (amps. × 10^{-4}/cm.^{2}).	Cathode potentials in N-$CoSO_4$ at 15°.				
	$N/10$-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.	p_H 6·0.
0·14	−0·19	−0·17	−0·19	−0·22	−0·24
0·56	−0·22	−0·22	−0·34	−0·39	−0·44
1·4	−0·31	−0·42	−0·49	−0·56	−0·56
2·8	−0·36	−0·46	−0·56	−0·57	−0·57
5·6	−0·42	−0·51	−0·57	−0·59	−0·59
12·0	−0·49	−0·56	−0·59	−0·61	−0·61
40·0	−0·56	−0·57	−0·61	−0·62	−0·63
80·0	−0·57	−0·59	−0·62	−0·63	−0·64
160·0	−0·58	−0·60	−0·63	−0·64	−0·65

TABLE VIII.

Deposition potential of cobalt from N-solutions.

Temperature	15°	55°	95°
Potential	−0·56	−0·46	−0·36
Overvoltage	0·25	0·15	0·05

The reversible potential of the electrode Co|N-$CoSO_4$ has been taken as − 0·31 volt (*Abh. Deut. Bunsengesellschaft*, No. 5, 1911), and the temperature coefficient has been neglected. The temperature coefficient of overvoltage of cobalt deposition is thus − 0·0025 volt/degree.

Discussion of Results.

The fact that the potentials at which the metals iron, nickel, and cobalt begin to be deposited are independent of the hydrogen-ion concentration of the electrolyte—within the range of p_H investigated, *i.e.*, roughly 2 to 6—throws doubt on some of the theories which have been suggested to account for the retardation of the deposition of these metals. In a N-solution of a simple nickel salt, the reversible potential is about − 0·24 volt; at this potential, the hydrogen pressure in the electrode is roughly equivalent to 10^4 atms. in a solution of p_H 2, and to 10^{-4} atm. in a solution of p_H 6. According to the views of Foerster (*loc. cit.*), Smits (*loc. cit.*), and Kohlschütter (*loc. cit.*), we should expect that the overvoltage of metal deposition would be affected by the concentration of hydrogen gas at the electrode, yet actually this does not appear to be so. The deposition potential, too, is probably not so much affected by the structure of the deposit as Kohlschütter imagines, because the presence of a depolariser (*e.g.*, hydrogen peroxide) causes scarcely any change in the deposition potential although it is said to influence the contraction of the deposit. If we accept the "hydride" theory of Frölich and Clark (*loc. cit.*), we also obtain conflicting conclusions. Since the minimum overvoltage of any metal is almost independent of the hydrogen-ion concentration of the electrolyte (J., 1924, **125**, 2414, 2646; and unpublished measurements with nickel, copper, tin, and cadmium), it may be inferred that the "hydride" has a fairly definite composition; the constancy of the deposition potential, however, would suggest that in the deposition of metal the composition of the "hydride" varies with the hydrogen-ion concentration of the solution. From Le Blanc's theory, we should expect not so much a large overvoltage for the initial deposition potential of the metal as a rapidly increasing polarisation with increasing *C.D.* and increasing rate of metal deposition. The *C.D.*–cathode potential curves should be of the type obtained by Spitzer (*Z. Elektrochem.*, 1905, **11**, 345) during the electrolysis of solutions of the complex cyanides of copper and zinc; the actual curves, however, are not at all of this type, for although an excess potential has to be applied in order to initiate deposition, yet the subsequent polarisation is very little more than that occurring during the deposition of mercury, lead, or copper from solutions of their simple salts. This serious objection to Le Blanc's theory probably applies also to the other reaction-velocity theories, for in every case we should expect the polarisation effect to increase rapidly with increasing rate of metal deposition.

As an alternative to the theories discussed above, the following tentative hypothesis is suggested. In the ions of iron, cobalt, and nickel, although the 3-quantum orbit of electrons is not completed, yet we know that there is a tendency for some additional electrons to go into a 4-quantum orbit. If when a nickel ion takes up two electrons at the cathode they both enter the 4-quantum orbit, then an atom with the electronic arrangement 2, 8, 16, 2 results; this metastable atom may have, like the zinc atom (2, 8, 18, 2), a strong tendency to lose its last two electrons, and so it would be a strongly electropositive metal having a deposition potential more negative than that of ordinary stable nickel, with a possible arrangement of 2, 8, 17, 1 * (compare Kramers and Holst, "The Atom and the Bohr Theory of Its Structure," 1923, p. 209). The metastable form would be transformed spontaneously, but at a definite rate, into ordinary nickel, and so the actual deposit would consist of a system of two forms of nickel; this system would be deposited at a potential lying between the reversible potential of ordinary nickel and that of the more electropositive unstable form, and thus an excess potential over that of ordinary nickel would be required before deposition could commence. There appears to be no reason why the composition of the deposited metal should vary appreciably with the *C.D.*, and so there should be no large polarisation effects

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* Russell (*Nature*, 1925, **115**, 455) has suggested that *ordinary* nickel has the arrangement 2, 8, 16, 2, whilst 2, 8, 17, 1 is that of *passive* nickel.

as the rate of metal deposition is increased; this is in agreement with the observed facts. The composition of the deposit should depend only on the rate of transformation of the unstable to the stable form of metal, and this will depend almost solely on the temperature; at each temperature, therefore, the deposit will have a definite composition and consequently a definite deposition potential dependent only on the concentration of metal ions in the electrolyte. At higher temperatures, the rate of transformation into the stable form will be increased and so the deposit will contain more ordinary nickel and the deposition potential will approach more and more the reversible nickel potential. These suggestions apply equally well to the deposition of iron and cobalt. The contraction observed in the electro-deposits of these three metals may be attributed partly to the change from unstable to stable form which occurs in the deposit subsequent to deposition; it is probable, however, that the simultaneous evolution of hydrogen has some influence.

Summary.

(1) By the use of the commutator-extrapolation method of measuring the potentials of polarised electrodes, the initial deposition potentials of iron, cobalt, and nickel have been measured at a number of temperatures in a series of solutions of varying hydrogen-ion concentration.

(2) The deposition potential has in each case been found to be independent of the hydrogen-ion concentration of the solution and of the anions present. Depolarisers, too, do not appear to affect the results.

(3) The theories which have been advanced to account for the retardation of the deposition of the iron-group metals are examined and found not to be in agreement with the observed facts.

(4) An alternative theory is suggested according to which the metals are primarily deposited in an unstable form with a different electronic arrangement from that of the ordinary form.

UNIVERSITY COLLEGE, EXETER. [*Received, September 2nd,* 1926.]