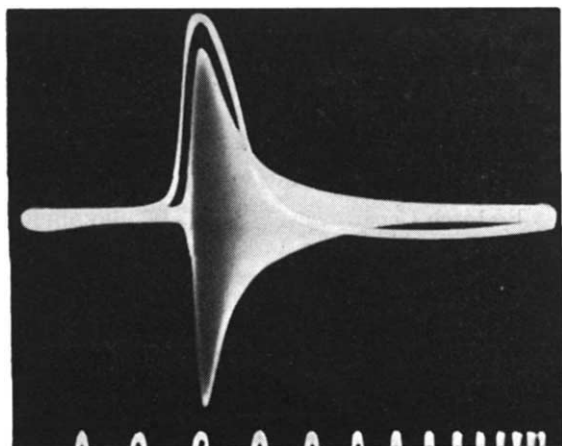


width is the record of a two per cent maximum unbalance of the bridge for a frequency of 20 kilocycles per second as the impulse came past the impedance electrodes. For reference, the action potential between an impedance electrode and an injured end was recorded on the same film immediately afterwards.

It can be shown that the bridge unbalance is nearly proportional to the change in membrane conductance, and the onset of the conductance increase here, as in *Nitella*, occurs somewhat after the start of the action potential, but coincides quite closely with the point of inflection on the rising phase.



IMPEDANCE CHANGE AND ACTION POTENTIAL OF THE SQUID GIANT NERVE FIBRE DURING THE PASSAGE OF A NERVE IMPULSE. INTERVAL BETWEEN TIME MARKS AT THE BOTTOM IS ONE MILLISECOND.

At this point, the membrane current density reverses in direction, corresponding to a decrease of the membrane electromotive force, so that this E.M.F. and the conductance are closely associated properties of the membrane, and their sudden changes are themselves, or are due to, the activity which is responsible for the propagation of the nerve impulse.

The capacity is probably a property of the ion-impermeable aspect of the membrane, while the conductance is due to the ion permeability. Since the maximum observed conductances are still far from a complete permeability, and because the capacity changes are relatively slight, we have indications that the excitation does not involve a disintegration or destruction of the membrane.

It is reasonable to suppose that similar changes occur in the membranes of smaller nerve fibres during excitation and the propagation of the nerve impulse.

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¹ Cole, K. S., and Curtis, H. J., *Cold Spring Harbor Symposia on Quantitative Biology*, 4, 73 (1936).

² Curtis, H. J., and Cole, K. S., *J. Gen. Physiol.*, 21, 189 (1937).

³ Curtis, H. J., and Cole, K. S., *J. Gen. Physiol.*, July 20, 1938.

⁴ Cole, K. S., and Curtis, H. J., *J. Gen. Physiol.*, to appear September 20, 1938.

⁵ To be submitted to *J. Gen. Physiol.*

Reduction of Ions of Nickel, Cobalt, Iron and other Metals by Zinc Amalgam

THE statement that a metal will always displace any other metal below it in the potential series from solutions of its salts is well known not to be true in practice. As an example, the standard way of reducing ferric to ferrous ions in acid solution by zinc ought to fail because, according to the statement, reduction should not stop at the ferrous stage, as it does, but continue to the metal, zinc standing much higher in the potential series than iron. In general it has been found that, provided the displacing metal is not passive, ions of metals of the B-subgroup of the periodic classification conform to the simple statement and those of the metals iron, cobalt, chromium, molybdenum, and other 'special-steel' metals do not. Thus zinc instantly reduces to metal the ions of cadmium, thallium and tin, but not those of chromium, iron, nickel, and cobalt, although chromium and iron are close to cadmium in the potential series, and nickel and cobalt lie below both thallium and cadmium. The accepted explanation of this anomaly which preserves a belief in the potential series of metals is that with these ions the expected reaction is retarded or inhibited by causes involving the phenomena of passivity, over-voltage or polarization. Experiments we have done seem to show, however, that the main cause of the anomaly lies in the existence of a protective ring of groupings around what is ordinarily regarded as the simple ion of a 'special-steel' metal.

There is no doubt of the slowness of the reduction to metal of some ions. In dilute sulphuric acid solution, ferrous sulphate is at least a thousand times more slowly reduced by zinc amalgam than are cadmium or copper sulphate solutions under similar conditions. Nickel and cobalt sulphate are from one hundred to five hundred times more slowly reduced than cadmium or copper sulphate. This slowness does not seem to be primarily due to a metal surface or to the fact that the zinc is present as an amalgam or to reaction between a partially deposited metal and the electrolyte. Similar differences in the rates of reduction are found when there is no metal present at all, when, for example, a solution of ter-valent uranium sulphate or chloride is used. This is the most powerful common reducing agent available as a solution, and reduces cadmium ions in dilute sulphuric acid instantly to metal. Yet its effect on nickel and cobalt ions in dilute sulphuric acid is extremely slow, and on ferrous, divalent chromium, or ter-valent titanium ions it is apparently nil.

These observations suggest that the main cause of the slowness lies not in the reducing agent but in the state of the ions to be reduced. This was confirmed by a number of experiments on cobalt, nickel, iron, titanium and other metal ions. It was found that when nickel, cobalt or iron were in the form of complex anions, reduction to metal by zinc amalgam sometimes took place rapidly. Thus from solutions containing ammonium sulphate and ammonium hydroxide in excess, nickel and cobalt are as rapidly reduced to metal by zinc amalgam as in like conditions is copper. Again, from the blue solution of cobalt chloride in concentrated hydrochloric acid, where the anion is believed¹ to be CoCl_4^- , cobalt is reduced to metal from the moment the zinc amalgam is brought in contact with the solution. (This is proved by the marked catalytic effect of metallic cobalt on

the production of hydrogen from zinc and acid.) But the apparently simple cobalt ion of the pink, aqueous or dilute acid solution is not reduced when the complex anion is. As the former is believed² to be $\text{Co}(\text{H}_2\text{O})_6^{++}$, it would appear that the groupings round the simple cation are the chief hindrance to the electrons which would convert the simple ion to metal atom. They guard the position which in the atom is occupied by the valency electrons. With complex anions, on the other hand, there is usually in equilibrium a small concentration of simple cation and this could be reduced to metal atom before it became ringed round with protective groupings.

That groupings surround the simple ions of metals like iron, cobalt, nickel, chromium, vanadium, titanium, etc., is on general grounds very probable. There is no difficulty in the reduction of any of the ions of higher state of oxidation of these metals. Quinque-, quadri- and ter-valent vanadium, for example, or ferric ion are, as is well known, easily reduced. But in these cases there are obvious vacant places inside the protected ion for the reducing electrons. It is at the final stage of reduction when the outer valency electrons have to be added that the protective effect of the groupings makes itself manifest.

From ammoniacal solutions, only nickel and cobalt were found to be reduced by zinc amalgam. From strongly acid solutions, nickel, cobalt and iron may all be obtained. The other metallic ions tried—those of titanium, vanadium, chromium, molybdenum and tungsten—were found not to yield more of the metal than was sufficient to show catalytic action on the evolution of hydrogen from zinc and acid, in confirmation of earlier work³. In general, the nickel and cobalt combine rapidly with the zinc to form compounds containing no mercury, of approximate formulæ ZnNi and ZnCo . The combination of iron with zinc occurs much more slowly. The product has the approximate formula ZnFe_7 .

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¹ Donnan and Bassett, *J. Chem. Soc.*, **81**, 939 (1902).

² Howell, *J. Chem. Soc.*, 2039 (1927).

³ Groves and Russell, *J. Chem. Soc.*, 2208 (1931).

Do Anthocyanins occur in Bacteria?

It has frequently been stated that colouring matters of anthocyanin type are produced by bacteria, and as there does not yet appear to be any justification for this view, it may be desirable to correct an error which is finding its way into the text-books¹. In most of the alleged instances of the occurrence of anthocyanins in micro-organisms, the description of the colouring matters and that of their reactions does not afford a *prima facie* case for their identification as members of the anthocyanin group, and there exists no example of the isolation and characterization from such sources of a substance which is undoubtedly an anthocyanin. Two publications, however, require more serious examination.

A. E. Kriss² has described a pigment of *Actinomyces Waksmanii* which is red in acid, blue in alkaline solution, and in these and other respects exhibits a superficial resemblance to an anthocyanin. We have made a culture of this or a closely related organism (probably *A. violaceus-ruber* Waksman), and from this have isolated in a crude form a pigment tallying in all respects with the description of Kriss. The

substance is not a glucoside and undoubtedly shows considerable superficial resemblance to an anthocyanidin (for example, malvidin chloride). It is, however, definitely not an anthocyanidin, and the conclusive proof of this is that its solution in aqueous sodium hydroxide is perfectly stable and maintains a pure royal blue colour after boiling for a considerable time. No substance containing a flavylum nucleus will withstand such treatment; the heterocyclic nucleus is invariably quickly ruptured by the action of strong alkalis with the formation of orange or yellow polyhydroxychalkone derivatives.

It should be noted that the chemistry of the flavylum salts, in so far as it relates to their behaviour in acid and cold alkaline solutions, is naturally very similar to that of other classes of basic dyes, such as the oxazines, thiazines and azines, which contain a suitably constituted heterocyclic nucleus associated with hydroxylated benzene rings. Thus a polyhydroxyphenazine might simulate an anthocyanidin in respect of its indicator reactions, and there is little reason to doubt that this interesting pigment of *Actinomyces* is derived from one of these more stable types.

It has also been claimed³ that, when *Bacillus citrulli* Sartoryi is cultured in a synthetic medium containing glucose and asparagine as sole sources of carbon and nitrogen, a triglucoside of pelargonidin is formed. The pigment was isolated and analysed and the aglucone, supposed to be pelargonidin chloride, was also analysed, the results tallying closely in both cases with those demanded by theory. Nevertheless, there are certain features of the description that suggest that this identification is erroneous and no direct comparisons were instituted; the absence of nitrogen was assumed after the failure of a qualitative test.

The object of this note is to emphasize that there is, as yet, no clearly proved case of the occurrence of anthocyanins in micro-organisms.

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¹ Cf., for example, Buchanan and Fulmer, "The Physiology and Biochemistry of Bacteria" (London, 1928); and Anderson, "An Introduction to Bacteriological Chemistry" (Edinburgh, 1938).

² *C. R. Acad. Sci. U.S.S.R.*, **4**, 283 (1936); *Brit. Chem. Abstr.*, **A**, 99 (1937).

³ Sevenet, J., Thesis, Strasbourg (1930).

Oestrogenic Activity of Esters of Diethyl Stilbæstrol

It is a well established fact that the esterification of naturally occurring oestrogenic substances such as oestrone and oestradiol causes a marked alteration in their biological activity, particularly with regard to the duration of their action. It was therefore decided to investigate the biological activity of various double esters of the synthetic oestrogenic agent diethyl stilbæstrol previously described by us¹.

The quantity of material administered was dissolved in 3 c.c. of sesame oil and given night and morning on three successive days to ovariectomized, inbred Wistar rats. Smears were taken after the third day and at intervals as long as oestrus persisted. From the accompanying table, it can be seen that esterification reduces the activity but that the effect