adrenalin (alkaloid), and tyramine acid phosphate cause vasoconstriction of the coronary vessels of the terrapin. Increased tonus, with tonus waves, is observed in the terrapin ventricles in some cases after the injection of pituitary extract and histamine.

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3243

Reduction Potentials of Organic Substances by the Lead Peroxide Electrode.

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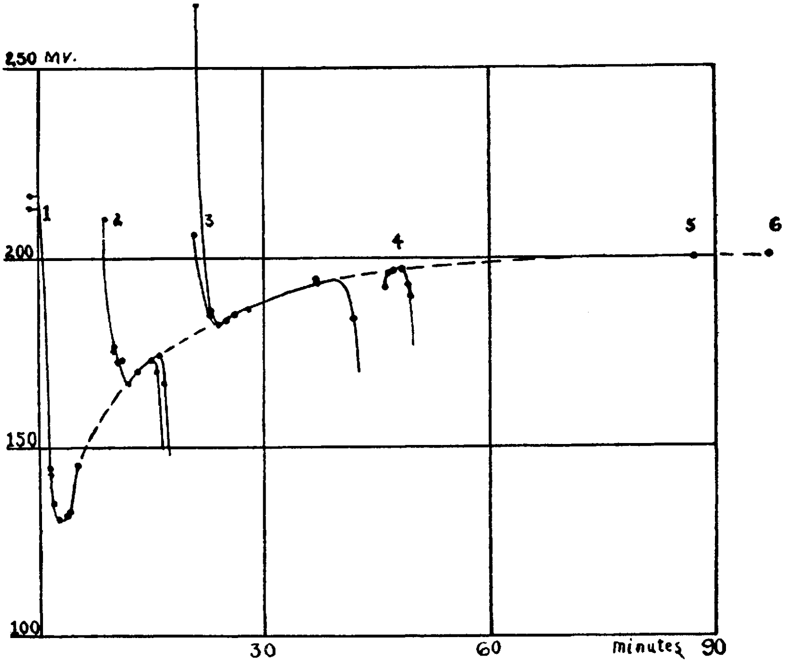
It has been pointed out frequently that the potentials measured in a solution of pure oxidant or pure reductant have a questionable meaning. Moreover such potentials are difficult to measure because they fall in a region of a curve approaching the potential axis asymptotically, and thus a slight change of conditions in the solution causes a wide fluctuation of potential. In such a solution an "inert" electrode, being unpoised, is subject to further fluctuation due to its own surface activity.

The same considerations obviously apply to solutions of those reductants which tend to transform irreversibly into products not active at an electrode, such as most organic compounds. Various schemes have been proposed for the measurement of such potentials, which depend in general upon the addition of some other component which poises the system.

It occurred to us that an oxidizing electrode might in itself have a poising action on an otherwise irreversible system. We have tried manganese dioxide and lead peroxide electrodes. In the following, we report preliminary determinations with lead peroxide electrode on solutions of certain organic reductants. The electrodes were prepared by plating out lead peroxide on platinum electrodes, made anodal in a solution of lead nitrate acidified with eight per cent nitric acid, under voltage sufficient to cause evolution of a fine stream of gas bubbles. These electrodes read in buffer solutions far in the the oxygen overvoltage region. On long standing they approach the oxygen electrode potential, but still read sluggishly in a reducing solution. If placed in a solution of a reducer until equilibrated, then washed in buffer until they again approach the oxygen electrode potential, when next placed in a reducing solution, equilibrium is attained very promptly. The lead is gradually reduced, but as long as the thinnest film remains on the platinum the potentials are constant and precise.

Curves may be plotted by inserting one pair of electrodes after another in the solution, replacing them when a sudden negative change of potential indicates that the platinum surface is exposed. A curve thus consists of a series of short curves, one segment of

FIG. 1.



Curve of potential of 0.1 M dihydroxy acetone at pH 11.3, T = 27° C., as recorded by the lead peroxide electrode. Each full line curve is that of a pair of electrodes, through a segment of which the broken curve can be drawn.

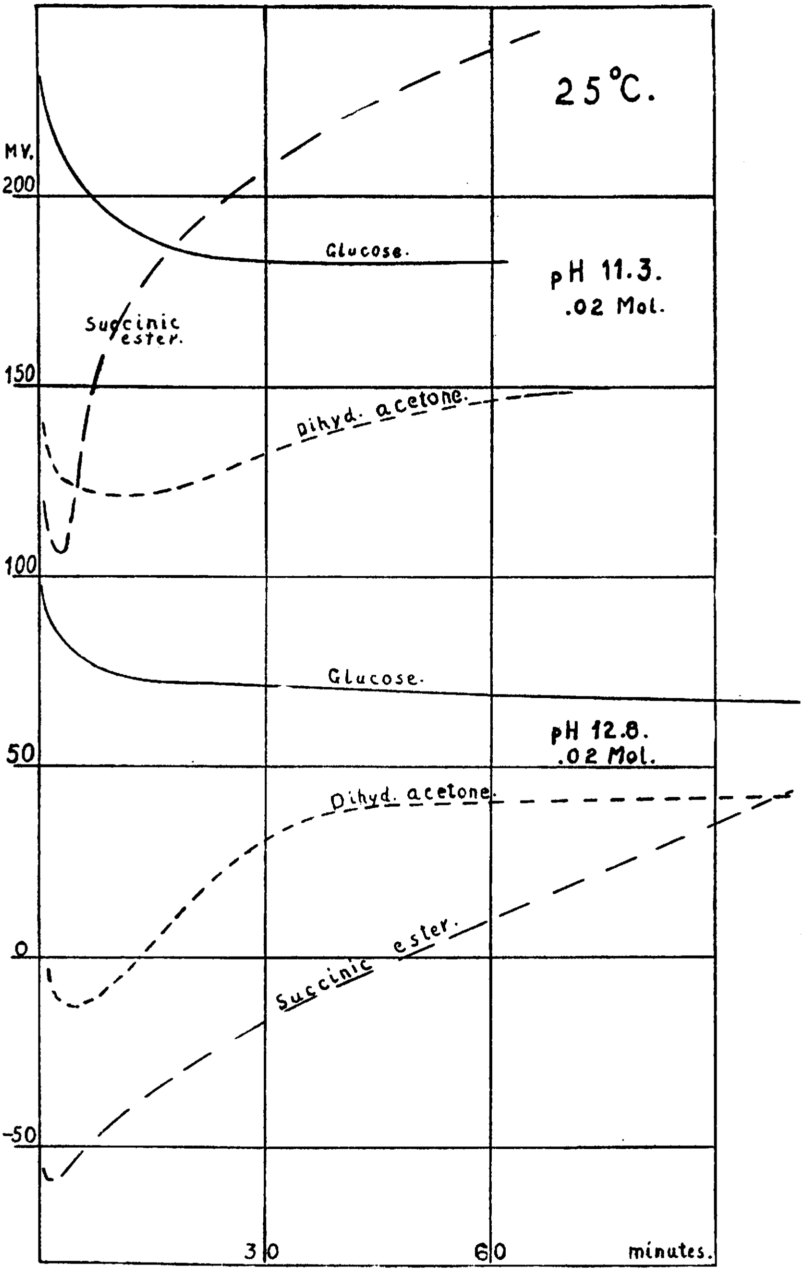
each of which represents equilibrium with the solution. (Fig. 1.) The electrodes are always prepared and used in pairs, and the readings of properly prepared electrodes at equilibrium conditions check to within one or two millivolts. Readings are made in vessels holding fifteen cc. of solution, through which a stream of commercial nitrogen, de-oxygenated by hot copper, stirs the solution and prevents the entrance of oxygen. The rubber stopper to this vessel carries two electrodes. Through a third hole, by which nitrogen is escaping, the capillary end of a tube containing the dry compound to be measured is inserted and nitrogen drawn through it. Then the oxygen free solution is drawn into the tube and allowed to flow back repeatedly until the material is washed into the electrode vessel.

The properties and mode of functioning of these electrodes may be tentatively described as follows:

The reducing substance in solution is a source of electrons which give rise, by reaction with plumbic ions at the electrode surface, to plumbous ions. The solution in the vicinity of the electrode tends to become saturated with both Pb^{++++} and Pb^{++}. When the solution is unstirred this constant concentration of both ions has a poising action on the potential, and enters as a constant into the potential reading.* The reducing substance also tends to give up electrons, through the electrode as a conductor, to the Hg^{+} of the calomel cell, and thus gives a negative potential to the lead peroxide electrode in proportion to the electron pressure of the reducing compound. This reduction potential is thus superimposed upon or added algebraically to that of the poised lead system ($Pb^{++++} + 2e \rightleftarrows Pb^{++}$). The potential measured, therefore, seems to be the resultant of all these forces, namely, the attractions of Hg^{+} and Pb^{++++} for the electrons of Pb^{++} and of the reducing compound. Since the values of Hg^{+}, Pb^{++++} and Pb^{++} are constant, the only variable is the electron pressure of the reducing substance.

In order to test the effect of plumbous ions at the electrode, we saturated the buffer used in certain experiments with $Pb(OH)_2$. The potentials of the unstirred solutions are approximately the same as before. Stirring now has almost no effect on the potentials of irreversible compounds. This indicates that one effect of stirring the solutions to which no $Pb(OH)_2$ has been added is to reduce the concentration of Pb^{++} ions at the electrode surface.

FIG. 2.



Curves of potential of organic reducing substances as recorded by the lead peroxide electrode. Potential as read against a N calomel cell. Further information in text.

Duplicate solutions, in one of which many electrodes are allowed to be reduced, in the other only one, register the same potential at the end. On the other hand, accumulation of reduced ions at the electrode surface should cause a negative potential, which should become more positive on stirring. This is what happens in most solutions, but a very slight stirring is as effective as a vigorous one in raising the potential. The electrodes are generally read under both conditions, stirred and stagnant, two parallel curves resulting. In solutions of reversible substances (ferrocyanide and hydroquinone), stirring lowers the potential instead of raising it, due to the removal of the oxidized form of the substance from the region of the electrode. One other substance which we have investigated (diacetyl succinic ester), also behaves in this way.

In figure 2 are presented curves of three of the compounds we have studied, at two pH levels, one buffer consisting of 0.4 M Na_2CO_3 plus 0.2 M KCl, of measured pH 11.3, the other of 0.1 M NaOH plus 0.9 M KCl, of measured pH 12.8; both are approximately 1.0 molar for the cations. The potentials are in millivolts as read against a 1.0 N calomel cell through a 1 N KCl bridge, the solution contact potentials being neglected for the time being. The electrode vessels are immersed in a water bath at 25° C. up to the levels of the contained solutions. The bath is electrically heated and controlled by an accurate thermostat.

The effect of higher concentration of the reductant is to render the potential more positive in the case of glucose and dihydroxy acetone, and more negative in the case of diacetyl succihic ester. Ferrocyanide and hydroquinone also act like diacetyl succinic ester, as they do also in the effect of stirring. The effect of more alkaline pH is to shorten the time dimensions of the curves of glucose and dihydroxy acetone, as well as to reduce the potential level. The effect on succinic ester is to lengthen the time coordinates of the curve, presumably due to a difference in the course and in the products of the reaction at different degrees of alkalinity.

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* Glasstone (*J. Chem. Soc.*, 1922, cxxi, 1469) found the half-cell $Pt+PbO_2$ (S) + PB (S) + NaOH (N) to be reversible and reproducible. He calculated the values 2.2×10^{-15} for $[Pb^{++}]$ and 1.3×10^{-65} for $[Pb^{++++}]$.