4. A freshly ignited platinum electrode, immersed in a solution of silver nitrate, usually acquires the electromotive behavior of silver. This is probably due to an invisible coating of that metal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE BEHAVIOR OF ELECTRODES OF PLATINUM AND PLATINUM ALLOYS IN ELECTROMETRIC ANALYSIS. II. POLARIZED ELECTRODES

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It has already been stated in Part I of this article[2] that the electrode system found most useful for determining the end-point in actual titrations consisted of two identical, pure platinum electrodes between which a very low polarizing current was allowed to flow continuously. The latter was obtained by applying a constant potential of from 0.20 to 1.00 volt and interposing a fixed resistance of 20,000 ohms in series with the two electrodes. Polarized electrodes have the great practical advantage of giving more definite and reproducible potentials than those given by the unpolarized electrodes described in the first article.

Such a polarized electrode system in contact with a solution of ferrous sulfate exhibits a difference in potential which decreases rapidly on the addition of a small amount of potassium permanganate. Near the completion of the oxidation the difference increases, rises very sharply as the last traces of ferrous ion are oxidized and decreases again as the excess of the oxidizing agent increases. The titration curve has, therefore, the same characteristics as the curve obtained for the same reaction with unpolarized electrodes under the conditions discussed in Part I. That the curve representing the potential difference between the polarized electrodes should resemble in a general way the similar curve for the unpolarized electrodes is only what would be expected, since in both cases the main determining factor is the change in the degree of reversibility of the electrode reactions as the titration progresses. The closeness of the resemblance, however, varies considerably with the nature of the reaction concerned.

In the titration of ferrous iron with permanganate, for example, the solution, except at the very start and near the end-point, contains both ferric and ferrous ion in appreciable concentrations. Since the reversibility of the ferric-ferrous electrode is relatively high, both anodic and cathodic polarization are practically destroyed and the electrodes show

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[2] THIS JOURNAL, **47**, 9 (1925).

little or no potential difference. As the end-point is approached ferrous ion disappears and permanganate ion appears and the potentials of both electrodes rise sharply. At this higher potential the depolarizing effect of ferric ion is too slow and weak to be felt, so that at the end-point, and just beyond, neither electrode is effectively depolarized. With increasing concentration of permanganate ion, however, the cathodic depolarization becomes fairly effective and as a result of the higher potential the manganous ion acquires the power to depolarize the anode. This accounts for the fact that the potentials tend to draw together again beyond the end-point.

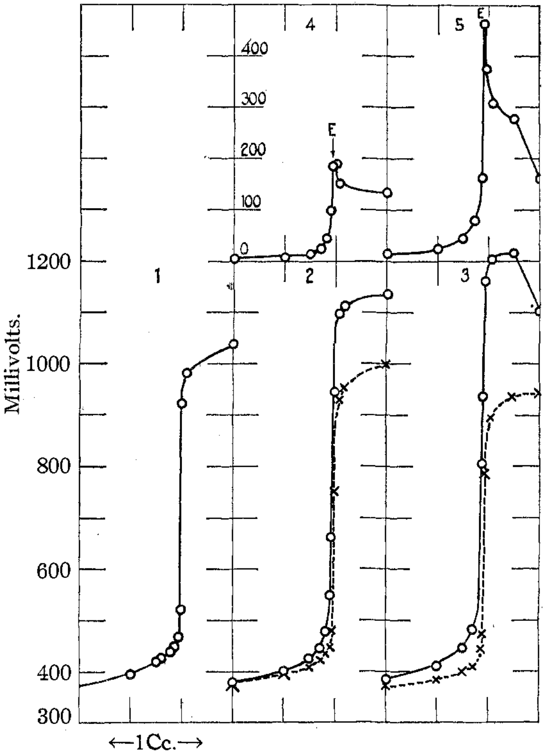

Fig. 1.—Titration of Fe^{++} with $KMnO_4$.

Solution, 0.008*M* $FeSO_4$, 0.9*M* H_2SO_4. Titrating solution, 0.01*M* $KMnO_4$. Applied polarization: Graph 1, 0.0 v.; Graph 2, 0.2 v.; Graph 3, 0.5 v.; Graph 4 is the difference curve for Graph 2 ($E_a - E_c$); and Graph 5, that for Graph 3.

In this and subsequent figures showing single electrode curves the behavior of the anode is indicated by a full line, the cathode by a broken line.

Fig. 1 gives the single potential curves for this reaction in the vicinity of the end-point only, and also the curves showing the difference in potential between the electrodes, $(E_a - E_c)$. On these and the following "difference curves" the end-point, as judged solely from the shape of the curve, is designated by E. This usage is slightly different from that of Part I.[2a] In the graphs of the single curves the behavior of the anode is indicated by full lines, the cathode by broken. The sharp fall in potential of the anode beyond the end-point, observed in this and in other cases in which the polarizing potential was 0.5 volt, or over,[3] is probably due to the deposition of a film of manganese dioxide on the anode after all the ferrous ion has been oxidized. A distinct darkening of the electrode was noticeable in these cases and it was proved by special tests that an electrode artificially coated with manganese dioxide gave a lower potential than did bright platinum.

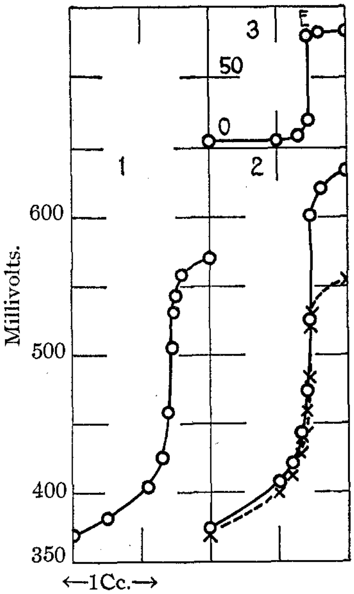

Fig. 2.—Titration of Fe^{++} with K$_2$Cr$_2$O$_7$.

Solution, 0.033*M* FeSO$_4$, 3.8*M* HCl. Titrating solution, 0.017*M* K$_2$Cr$_2$O$_7$. Applied polarization: Graph 1, 0.0 v.; Graph 2, 0.5 v; Graph 3 is the difference curve for Graph 2.

The titration of iron with dichromate, Fig. 2, is another example of the same type. The fact that the dichromate electrode is less reversible than the permanganate electrode was shown plainly by the much smaller tendency for the curves to draw together beyond the end-point. A reduction reaction in which the reversibility is high before the end-point, and much lower beyond it, is the titration of ferric iron with trivalent titanium, shown in Fig. 3. In all three of these cases the end-point is marked by a sudden rise in the potential difference between the electrodes.

An example of the reverse type, where the electrode reactions are nonreversible before the end-point but reversible beyond it, is given by the titration of thiosulfate with iodine, Fig. 4. In this case the polarized electrodes show a difference in potential up to the end-point where the difference suddenly falls to zero. The precipitation of zinc ion by potassium ferrocyanide, Fig. 5, is a reaction of approximately this same type because of the presence of a small amount of ferricyanide in the titrating solution. The potential difference decreases sharply at the end-point

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[2a] This Journal, **47,** 14 (1925).

[3] Fig. 6.

but does not disappear entirely. It could, no doubt, be made to disappear by using a mixture of ferro- and ferricyanide as the titrating solution, as has been suggested.[4]

Cases like these just considered, in which the reaction has a high reversibility on one side of the end-point and limited reversibility on the other, make up a considerable fraction of the oxidation-reduction reactions that are useful in volumetric analysis and it is evident that with this type of reaction in general polarized electrodes may be expected to give a definite upward or downward break at the end-point.

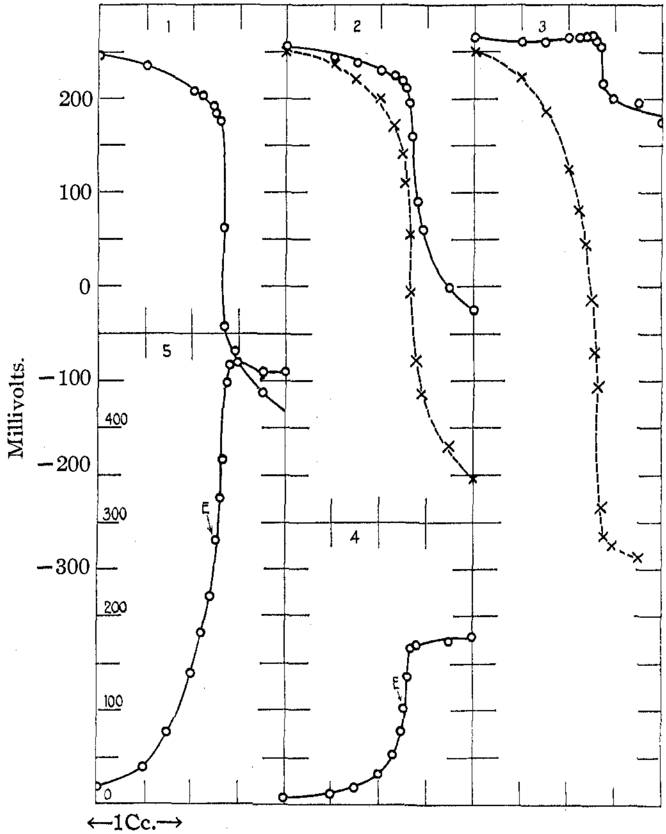

Fig. 3.—Titration of Fe^{+++} with Ti^{+++}.

Solution, 0.005*M* $Fe_2(SO_4)_3$, 1.2*M* H_2SO_4. Titrating solution, 0.03*M* $Ti_2(SO_4)_3$. Applied polarization: Graph 1, 0.0 v.; Graph 2, 0.2 v.; Graph 3, 0.5 v; Graph 4 is the difference curve for Graph 2; and Graph 5, that for Graph 3.

When the reversibility is limited on both sides of the end-point, the de-

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[4] Kolthoff, *Rec. trav. chim.*, **41,** 425 (1922).

termination of the end-point by the use of polarized electrodes may or may not be practicable. Such reactions are frequently incomplete or slow, and therefore available for volumetric analysis only in an indirect method, if at all. The titration of dichromate with sulfite is an example. With polarized electrodes no end-point break is obtained when the sulfite is added slowly, although an apparent end-point, variable in position with the speed of the titration, may be observed when the addition of the sulfite is sufficiently rapid.

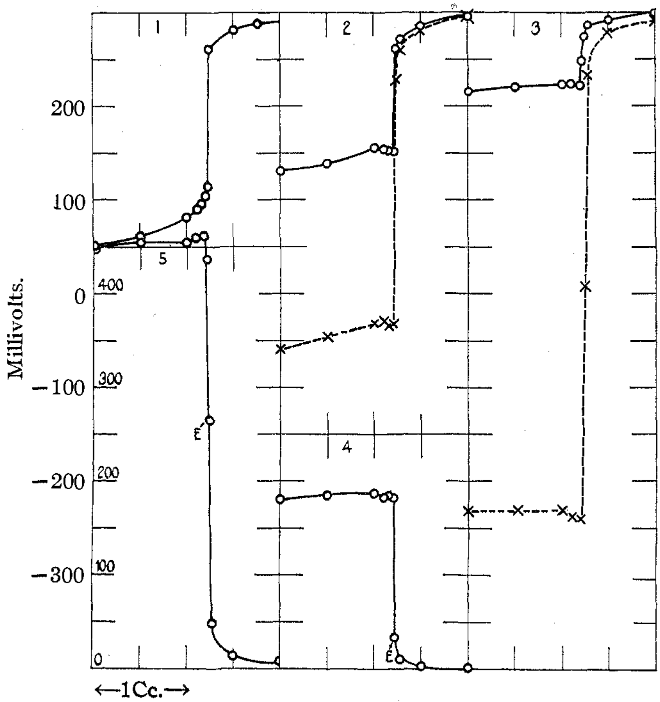

Fig. 4.—Titration of $Na_2S_2O_3$ with I_2.
Solution, 0.01*M* $Na_2S_2O_3$. Titrating solution, 0.05*M* I_2. Applied polarization: Graph 1, 0.0 v.; Graph 2, 0.2 v.; Graph 3, 0.5 v.; Graph 4 is the difference curve for Graph 2; and Graph 5, that for Graph 3.

In this group, however, there are a number of reactions with which polarized electrodes give sharp end-points. Two of these are shown in Figs. 6 and 7. The oxidation of hydrogen peroxide with permanganate, Fig. 6, is somewhat slow near the end-point, but when the titration is not carried out too rapidly the end-point is definite and reproducible. Fig. 7 shows the titration of tetravalent cerium with trivalent titanium. The relatively poor depolarization of the anode by an excess of the titanous sulfate is rather surprising. Notwithstanding its strength as a reducing agent it does not undergo anodic oxidation as readily as might be expected.

The possible case of a reaction in which the electrode potentials have a high degree of reversibility on both sides of the end-point can be very briefly dismissed, for it is doubtful whether a case of this kind exists in which the equilibrium lies near enough to one side to meet the requirements of an analytical method. Moreover, it is evident that in such a case the use of polarized electrodes would be impracticable. Depolarization would be nearly complete throughout the reaction and there would be no appreciable break at the end-point.

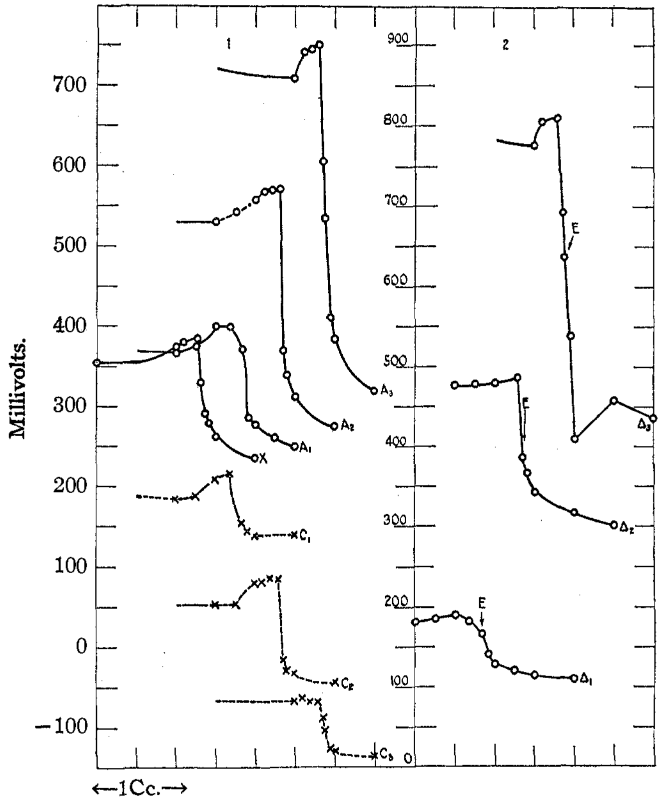

Fig. 5.—Titration of Zn^{++} with $K_4Fe(CN)_6$.

Solution, 0.015*M* $ZnSO_4$, 1.0*M* NH_4Cl, 0.6*M* HCl. Titrating solution, 0.05*M* $K_4Fe(CN)_6$. Applied polarization: Graph 1: Curve **X**, 0.0 v.; Curves A_1 and 1, 0.2 v.; Curves A_2 and C_2, 0.5 v.; Curves A_3 and C_3, 1.0 v. Graph 2: Curve Δ_1 is the difference; Curve for A_1, C_1; Curve Δ_2, for A_2, C_2; and Curve Δ_3, for A_3, C_3.

A comparison of the form, as shown in the graphs, of the single-potential curves with and without polarization, shows that in some cases the polarization has increased the magnitude of the end-point break. This indicates that polarization (with respect to an auxiliary platinum electrode) will in some cases improve the end-point break in titrations of the ordinary type, that is, those based on measurement of the e.m.f. between an inert electrode and a constant normal electrode. This expedient has been found

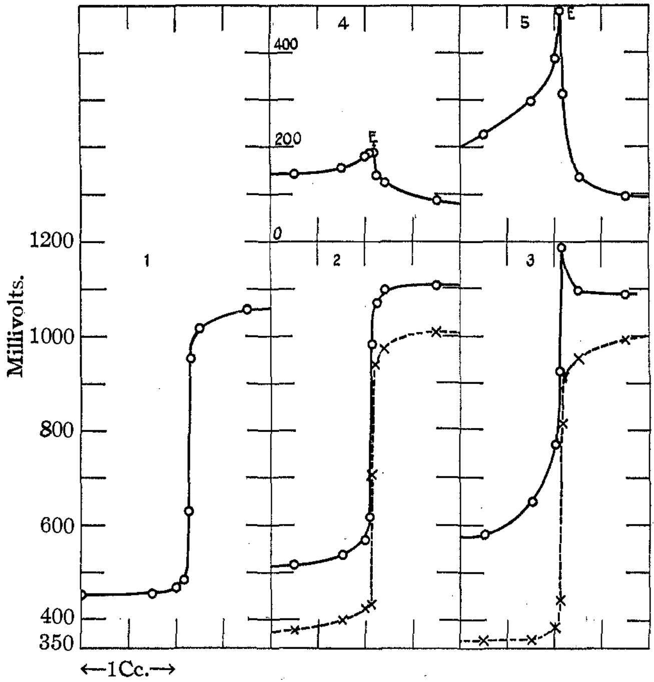

Fig. 6.—Titration of H_2O_2 with $KMnO_4$.
Solution, 0.012*M* H_2O_2, 0.9*M* H_2SO_4. Titrating solution, 0.01*M* $KMnO_4$. Applied polarization: Graph 1, 0.0 v.; Graph 2, 0.2 v.; Graph 3, 0.5 v.; Graph 4 is the difference curve for Graph 2; and Graph 5, that for Graph 3.

Table I

Effect of Polarization on the Single Electrode Break

Reaction	Anode	Cathode
Fe^{++}—MnO_4^-	Increased	Decreased
Fe^{++}—$Cr_2O_7^{--}$	Increased	Decreased
Fe^{+++}—Ti^{+++}	Decreased (more than cathode increased)	Increased
$S_2O_3^{--}$—I_2	Much decreased	Much increased
Zn^{++}—$Fe(CN)_6^{----}$	Considerably increased	Somewhat decreased
H_2O_2—MnO_4^-	Somewhat decreased	Little changed
Ce^{++++}—Ti^{+++}	Somewhat decreased (negligible, compared with total break)	Little changed

to be of great practical value, both because of the sharper break and because polarized electrodes in general give potentials that are more definite and less subject to annoying variations dependent upon the pretreatment of the electrode. For this reason it is often useful even in cases where the magnitude of the break is not appreciably increased. Table I gives a summary of the results of polarization on the single break for the various reactions studied.

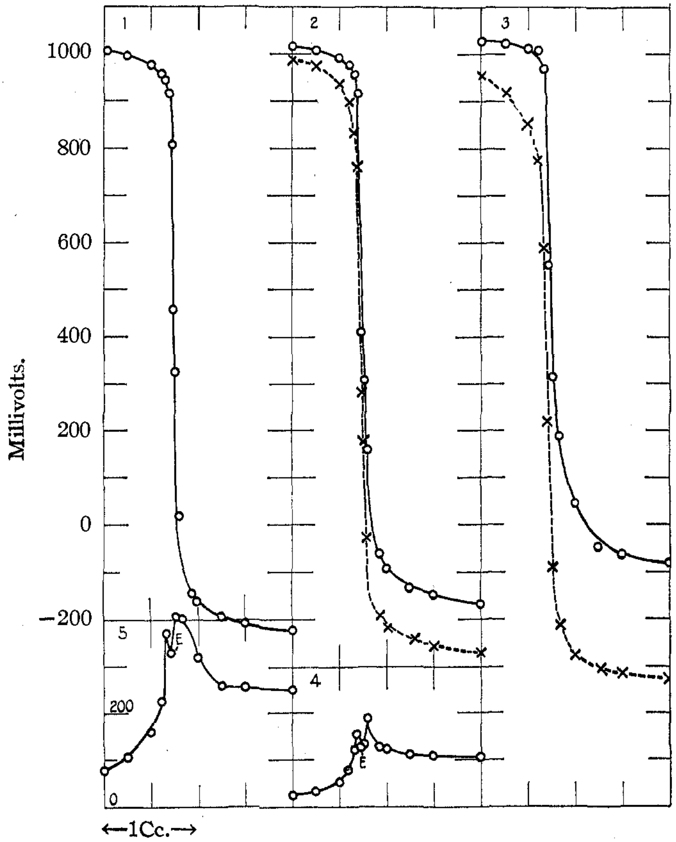

Fig. 7.—Titration of Ce^{++++} with Ti^{+++}.

Solution, 0.006*M* $Ce(SO_4)_2$, 1.0*M* H_2SO_4. Titrating solution, 0.03*M* $Ti_2(SO_4)_3$. Applied polarization: Graph 1, 0.0 v.; Graph 2, 0.2 v.; Graph 3, 0.5 v; Graph 4 is the difference curve for Graph 2; and Graph 5, that for Graph 3.

These results show that polarization has a greater effect upon the single electrode potentials, the more nearly the reaction in question approaches to complete reversibility on one side of the end-point and to complete irreversibility on the other. It is also evident that to increase the magnitude

TABLE II

DISPLACEMENT OF SINGLE ELECTRODE BREAK BY POLARIZATION

Reaction	End-point det. by	Position of end-point for applied potential—volts				M conc. titg. soln.	Behavior E_a-E_c in vicinity of e.-p.	Analysis of conditions
		0.0	0.2	0.5	1.0			
Fe^{++}—MnO_4^-	E_a	24.00	24.00	23.87	...	0.01	Rises to a maximum, then decreases.	Near e.-p., concn. of Fe^{+++} high, of Fe^{++} low. Cathodic depolarization good, anodic poor. Hence cathode behavior more nearly normal; anode break occurs too early.
	E_c	...	24.00	23.94	...	..		
	E_a—E_c[a]	...	24.00	23.90	...	..		
Fe^{++}—$Cr_2O_7^{--}$	E_a	...	...	25.44	...	.017	Rises sharply at e.-p.	Same as above.
	E_c	...	...	25.46	...	..		
	E_a—E_c[b]	...	...	25.46	...	..		
Fe^{+++}—Ti^{+++}	E_a	25.63	25.68	25.70	...	.03	Increases sharply at e.-p.	Depolarization at anode good; at cathode poor. Cathode break occurs too early.
	E_c	...	25.62	25.55	...	..		
	E_a—E_c[b]	...	25.62	25.55	...	..		
$S_2O_3^{--}$—I_2	E_a	24.45	24.45	24.48	...	.05	Falls sharply at e.-p.	Depolarization at anode good, due to I^-; at cathode poor. Anode break probably more nearly correct.
	E_c	...	24.45	24.48	...	..		
	E_a—E_c[b]	...	24.45	24.48	..	..		
Zn^{++}—$Fe(CN)_6^{----}$	E_a	20.63	20.67	20.70	20.75	.05	Falls sharply at e.-p.	Small amounts of ferri- and ferrocyanide present throughout; breaks at anode and cathode agree.
	E_c	...	20.67	20.70	20.75	..		
	E_a—E_c[b]	...	20.67	20.70	20.75	..		
H_2O_2—MnO_4^-	E_a	...	24.15	24.10	...	.01	Rises to a maximum, then decreases.	Depolarization at both electrodes poor. Anode break probably more nearly correct.
	E_c	...	24.18	24.15	...	..		
	E_a—E_c[a]	...	24.15	24.10	...	..		
Ce^{++++}—Ti^{+++}	E_a	15.47	15.46	15.44	...	.03	Rises sharply just before e.-p., falls at e.-p., then rises sharply again in excess.	Unusual case. Anode increases in reversibility just at e.-p., then decreases again.
	E_c	...	15.43	15.40	...	..		
	E_a—E_c[c]	...	15.46	15.44	...	..		

[a] End-point determined by maximum of curve.

[b] End-point determined by point of inflection.

[c] End-point taken as midway between the two maxima.

of the break the electrode should be polarized in the direction in which depolarization is least effective on the irreversible side of the end-point.

Up to a certain point the break can be increased by increasing the polarizing potential, but too high a potential has a tendency to make the bend at the beginning of the break less abrupt and the break less vertical, so this expedient must be used with caution.

Displacement of Break by Polarization

In consequence of the effect just mentioned, the break with a polarized electrode does not always exactly coincide with the end-point as given by an unpolarized electrode. Thus in an oxidation reaction anodic polarization would tend to make the apparent end-point too early and cathodic polarization to make it too late. The magnitude of this effect would be less, the greater the reversibility in the end-point region.

Various instances of such displacement are visible in the graphs and these are summarized in Table II.

The conclusion to be drawn is that the displacement, from a practical standpoint, is not serious and that the error involved in determining the end-point from the titration curve, $E_a - E_c$, is well below the equivalent of 0.05 cc. of 0.1 *N* titrating solution.

Effect of Rate of Stirring

The efficiency of depolarization depends, among other factors, upon the concentration of the depolarizer at the surface of the electrode and this in turn upon the efficiency of the stirring. As a rule, therefore, the rate of stirring will have some effect upon the electrode potential.

This point was tested with a number of the reactions mentioned above. The potential changes were small in all cases, often unobservable and always negligible as regards their effect upon the end-point break. The most marked results were obtained with a solution approximately 0.001 *M* with respect to iodine and potassium iodide and 0.9 *M* with respect to sulfuric acid. They are given in Table III.

TABLE III

EFFECT OF STIRRING

Applied potential Volts	E_a Mv.	E_c Mv.	R.p.m.
1.0	313	252	200
	309	280	600
0.5	303	252	200
	300	278	600

Since the depolarization is improved by increased stirring, the two electrode potentials should be affected in opposite directions, as is actually observed.

Summary

1. The principal factor determining the sharpness of the electrometric end-point with polarized electrodes of pure platinum is the difference in the degree of reversibility of the electrode reaction before and after the end-point. Other factors such as concentration and rate of stirring are of minor importance. The end-point phenomena are more distinct, the more nearly the electrode reactions conform to the requirement of complete reversibility on one side of the end-point and complete irreversibility on the other, but are sharp enough for practical use in analysis in some cases which fall far short of meeting this requirement.

2. Although the polarization sometimes produces a slight displacement of the end-point break of a single electrode, the errors so introduced are generally too small to be of significance in a volumetric analysis.

3. The end-point break in titrations of the ordinary type, based on the single potential of a platinum electrode, may often be improved and the behavior of the electrode made much more dependable and satisfactory by polarizing it with respect to an auxiliary electrode.

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[Contribution from the Physical and Chemical Laboratories of the Ohio State University]

SOLID SOLUTIONS OF THE ALKALI AND AMMONIUM HALIDES

By R. J. Havighurst, E. Mack, Jr. and F. C. Blake

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The purpose of this paper is to establish the limits of miscibility of the alkali and ammonium halides at room temperature and to determine the natures and structures of their solid solutions. The photographic powdered-crystal method of X-ray analysis was employed. The apparatus and method of procedure for precision work have been described.[1] The constitution of metallic alloys has been frequently investigated by the X-ray method, but Vegard[2] seems to have been the only one to have used this procedure in the investigation of solid solutions of salts.

The problem of the miscibility of the alkali halides has often been studied by thermal and optical methods. These methods sometimes lead to ambiguous results, and are not always sufficient to permit definitely deciding whether a pair of salts is miscible at room temperature. X-ray methods, on the other hand, are capable of giving a definite answer to this question, provided only that the system be in equilibrium.

The Nature of Solid Solution.—Solid solution may take place in two different ways. The mechanism of the simpler of these two ways is a more

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[1] Havighurst, Mack and Blake, This Journal, **46**, 2368 (1924).

[2] Vegard, *Z. Physik*, **5**, 17 (1921).