

According to Crompton's hypothesis,¹⁰ alcohol and acetone should have practically the same latent heats of fusion, as their melting points lie so close together. Actually, that of acetone is 20% higher. In the equilibrium, liquid-solid, energy is also required to overcome molecular cohesive force when the solid changes into a liquid and the molecular surface energy of acetone is considerably greater than that of methyl alcohol.

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Summary

1. A method for the measurement of specific heats and latent heats of fusion at low temperatures, has been described.
2. The specific heats of ice, benzene, methyl alcohol and acetone were determined from -183.6° to their respective melting points.
3. The specific heat of ice was determined with particular care and the empirical formula, $c = 0.485 + 0.000914t - 0.00000546t^2$ found to express the relation between specific heat and temperature.
4. The average specific heats of phenol, *p*-xylene, naphthalene and benzophenone were determined over the range -183.6° to -78.2° .
5. The latent heats of fusion of water, benzene, acetone and methyl alcohol were determined.
6. Further evidence has been advanced to prove that atomic heat is a highly constitutive property, where the specific heat of a compound varies greatly with the temperature.

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THE BEHAVIOR OF ELECTRODES OF PLATINUM AND PLATINUM ALLOYS IN ELECTROMETRIC ANALYSIS. I DISSIMILAR ELECTRODES

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It has recently been shown² that the end-point in certain reactions may be determined with sufficient accuracy for analytical purposes by observing the accompanying sudden change in the difference in potential between two inert electrodes of different metals or alloys immersed directly in the solution. Even better results were obtained when the electrodes were both of the same material (pure platinum) and their dissimilarity was arti-

¹⁰ Crompton, *Proc. Chem. Soc.*, **65**, 240 (1895).

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² Willard and Fenwick, *THIS JOURNAL*, **44**, 2504 (1922).

ficially produced by polarizing with a potential of 0.2 to 0.5 volt through a resistance of 20,000 ohms.³ The present work is a more detailed study of such inert electrode systems and the conditions governing their potential differences. This paper, Part I, deals with the results obtained with dissimilar electrodes; Part II, to follow in a second article, will take up the case of polarized electrodes.

When two electrodes, one of pure platinum and the other of an alloy of platinum and rhodium, such, for example, as the usual thermocouple alloy containing 10% of rhodium, are dipped in a solution of ferrous sulfate, an appreciable difference in potential is observed. When a small amount of the ferrous salt is now oxidized the electrodes come to practically the same potential, and this relation is maintained until the oxidation is nearly complete, when the potentials once more diverge and with extreme rapidity as the true end-point is approached.⁴

This behavior may fairly be regarded as typical. With other reducing agents and other (inert) electrode materials the results approximate to those just given although, as would naturally be expected, a close agreement is found only in cases in which the reducing agent and its oxidation product form a system capable of giving reversible electrode potentials, like the ferrous-ferric ion mixture.

The two most probable causes for differences in potential between two "inert" electrodes are (a) failure of the electrodes to function as strictly unattacked, and (b) imperfect reversibility of the electrode reaction itself. It is very probable that the second cause is the important one here. Equilibrium at the electrodes is not fully maintained during the titration and the resulting lag differs in magnitude at the two electrodes.

Since the ideal expression for the electrode potential E , of an inert electrode, is of the form $E = \text{const.} \times \log \frac{x}{1-x}$ (x representing the fraction of the active agent which is in the higher stage of oxidation and $1-x$ that in the lower), its value will be exceedingly sensitive to slight changes in x when the latter approaches its limiting values 0 and 1, that is, near the beginning and again near the end of the oxidation, the analytical end-point.

If, in an actual titration, there is an appreciable lag in the electrode potentials its amount will tend to be different at the two dissimilar electrodes, and the divergence so produced will obviously be greatest in the regions of sensitivity just referred to. This effect is in fact observed in most cases at the end-point. Its appearance at the beginning of the titration is less generally observed, partly because it is not easy in all cases to obtain the reducing agent in a state of purity high enough to place the

³ Ref. 2, p. 2516.

⁴ Ref. 2, p. 2513; Fig. 5, p. 2509.

equilibrium within the very sensitive region, and partly because the phenomenon is often masked by limited reversibility of the electrode reaction, which prevents the potential difference from disappearing near the middle of the oxidation, as it does with the ferrous-ferric ion mixture.

If the above explanation is correct the potentials of the two electrodes should approach a common value with time. A large number of experiments were made to test this point, chiefly with the following reactions: titration of ferrous iron with permanganate, ferrous iron with dichromate, and thiosulfate with iodine, the electrodes being always of pure platinum and platinum-rhodium thermocouple wire, respectively, and the solutions mechanically stirred. The potential difference always tended to disappear, but in many cases persisted, at least in part, over long periods, and was not entirely destroyed even by short-circuiting the electrodes for some time. Only in solutions giving a reversible electrode reaction did the electrodes reach approximately the same potential, but the tendency was unmistakably in that direction, as called for by the explanation offered above. To obtain decisive results it was also necessary for the value of x to be very near one of its limiting values, a condition which is not always easy to fulfil in practice.

TABLE I

DECREASE IN POTENTIAL DIFFERENCE WITH TIME

0.025 M FeSO ₄ , ^a 1.5 M H ₂ SO ₄ Atmosphere of CO ₂		0.025 M Fe ₂ (SO ₄) ₃ , 1.5 M H ₂ SO ₄ , 5 × 10 ⁻⁷ M KMnO ₄	
Time Min.	E _{PtRh} - E _{Pt} Mv.	Time Min.	E _{PtRh} - E _{Pt} Mv.
0	128.5	0	267.5
3	93.2	8	299.5
10	58.0	19	316.5
16	19.2	59	206.5
21	0.0	104	29.0
		163	5.0
		213	1.0
0.025 M FeSO ₄ , 1.4 M HCl Atmosphere of CO ₂		0.025 M Fe ₂ (SO ₄) ₃ , 1.4 M HCl, 5.5 × 10 ⁻⁷ M K ₂ Cr ₂ O ₇	
0	169.5	0	13.4
2	89.5	10	7.0
4	16.5	21	3.0
11	0.0	40	1.5
		45	0.0
0.025 M KI, 0.012 M H ₂ SO ₄		0.012 M H ₂ SO ₄ , partly saturated with iodine. Atmosphere of CO ₂	
0	5.0	0	2.9
3	3.5	3	3.1
8	2.5	11	1.2
40	1.9	15	0.3

^a All concentrations are expressed in moles per liter.

Table I shows the time effect as observed with a number of solutions having compositions lying within the regions of sensitivity.

Further light on the phenomenon was sought by following the change in potential of both electrodes in several different reactions, especially in the region very close to the end-point. The electrodes were of pure platinum and the 10% rhodium alloy in the form of wires of 0.74mm. and 0.60-mm. diameter, respectively, and extended into the solution a distance of 2 to 4 cm. They were ignited at the highest temperature of a Méker burner just before use and were frequently cleaned with fused potassium bisulfate during the course of the work. The reference electrode used throughout the work was a 0.1 *M* silver chloride electrode of the type described elsewhere.⁵ Where not otherwise stated the numerical values of the potentials given in this paper are referred to the silver chloride electrode as zero and would be 0.29 volt higher if referred to the hydrogen normal electrode. All potential measurements were made with a Leeds and Northrup Type K potentiometer. The stirrer was of glass and motor driven.

In these experiments the titrating liquid was rather dilute to permit a sufficiently gradual approach to the end-point and the changes in potential were observed for a considerable time after each addition of the reagent.

Fig. 1 shows graphically the effects observed in the titration of a solution of ferric sulfate with permanganate. The solution probably contained some ferrous salt, for Hostetter and Roberts found ferrous iron invariably present in ferric solution.⁶ It should be borne in mind that the total amount of permanganate added in this experiment was equivalent to only 0.01 cc. of the usual 0.1 *N* solution. The true end-point of the titration undoubtedly lies within this range but the results do not suffice to show its exact position. It is evident that after each addition of permanganate both electrodes show a sharp rise in potential followed by a slower fall, both rise and fall being much greater with the platinum-rhodium electrode than with the pure platinum. The experiment was carried out several times with results very similar to those given here. In general the behavior of this platinum-rhodium electrode as observed in many experiments may be summed up in the statement that it appeared to come into equilibrium with a solution of increasing oxidizing power (or decreasing reducing power) more rapidly than the pure platinum and conversely. As a rule, therefore, this electrode showed a higher potential than platinum both in oxidation and reduction reactions. This was always true at the end-point, although there were a few exceptions when the oxidizing or reducing agent was present in appreciable excess. It should be emphasized, however, that the potentials of inert electrodes (except in solutions which

⁵ Ref. 2, p. 2508, Footnote 4.

⁶ Hostetter and Roberts, *THIS JOURNAL*, **41**, 1348 (1919).

give reversible electrode reactions) are subject to variations depending on the previous use of the electrode and on other factors which are unknown or difficult to control. For this reason anomalous results are common, and the interpretation of experimental data often presents serious difficulties.

The exact cause of the above-mentioned fall in the potential of both electrodes with the time is uncertain, but the fact, confirmed by a number of other experiments, that this fall is conspicuous only near the end-point, seems to justify the conclusion that it is due to an actual loss in the oxidizing power of the solution resulting from decomposition or other sec-

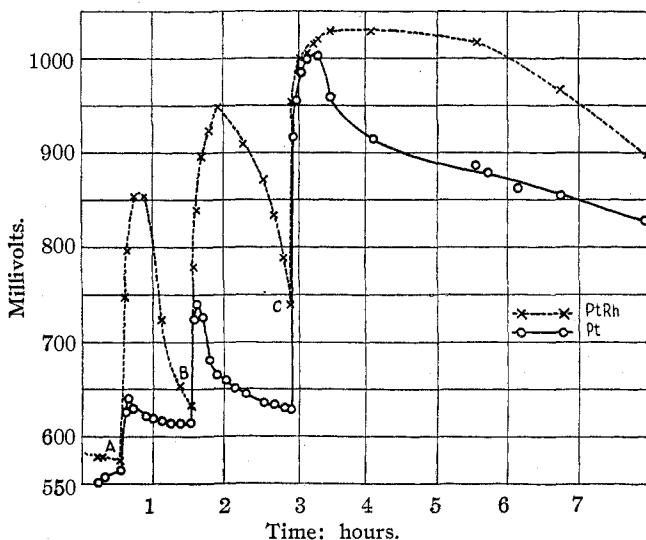


Fig. 1.—Variation of potential with time.

Solution, 0.008 M $Fe_2(SO_4)_3$, 0.9 M H_2SO_4 .

At Point A, 0.25 cc. of 0.0002 M $KMnO_4$ was introduced; at Point B, 0.10 cc.; at Point C, 0.65 cc.

ondary reaction, which although small in actual amount, is important at this point of extreme sensitivity. This does not, however, account for the fact that in a number of instances the potential of the platinum began to fall before the platinum-rhodium electrode attained its maximum.

Experiments like that of Fig. 1, in which other oxidizing agents were employed in place of permanganate, gave results of the same general nature, but the potentials near the end-point showed much less tendency to fall with the time.

Figs. 2 and 3 show the behavior of the same pair of electrodes in several titrations of different types, carried out at the rate of an ordinary analysis. The ordinates are the potentials of the two inert electrodes, the abscissas

cubic centimeters of the titrating solution. The graphs cover only the portions of the titration adjacent to the end-point. A curve showing the difference in potential between the two electrodes ($E_{\text{PtRh}} - E_{\text{Pt}}$), hereafter called the "difference curve," is also plotted. The end-point E , as marked on these difference curves, is shown in the position determined by the single electrode potentials. Its position does not differ in any of these cases by

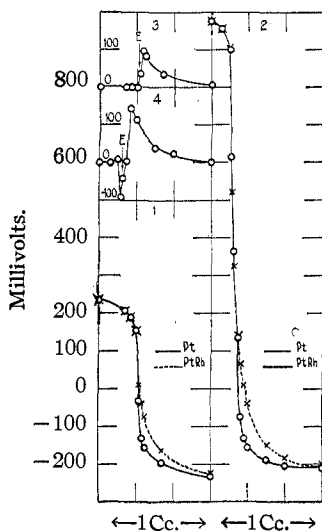


Fig. 2.—Graph 1. Titration of Fe^{+++} with Ti^{+++} . Solution, $0.017 M \text{Fe}_2(\text{SO}_4)_3$, $1.2 M \text{H}_2\text{SO}_4$. Titrating solution, $0.14 M \text{TiCl}_3$.

Graph 2. Titration of Ce^{++++} with Ti^{+++} . Solution, $0.006 M \text{Ce}(\text{SO}_4)_2$, $1.0 M \text{H}_2\text{SO}_4$. Titrating solution, $0.03 M \text{Ti}_2(\text{SO}_4)_3$.

Graph 3. Difference curve for Graph 1. ($E_{\text{PtRh}} - E_{\text{Pt}}$).

Graph 4. Difference curve for Graph 2.

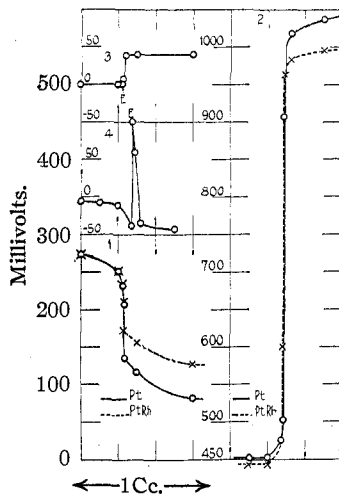


Fig. 3.—Graph 1. Titration of I_2 with $\text{Na}_2\text{S}_2\text{O}_3$. Solution, $0.01 M \text{I}_2$. Titrating solution, $0.05 M \text{Na}_2\text{S}_2\text{O}_3$.

Graph 2. Titration of H_2O_2 with KMnO_4 . Solution, $0.005 M \text{H}_2\text{O}_2$, $0.75 M \text{H}_2\text{SO}_4$. Titrating solution, $0.01 M \text{KMnO}_4$.

Graph 3. Difference curve for Graph 1.

Graph 4. Difference curve for Graph 2.

more than the equivalent of 0.05 cc. of 0.1 *N* titrating solution from the one that would have been chosen from inspection of the difference curve alone.

In the titration of ferric sulfate by titanous chloride⁷ (Fig. 2), all difference in potential between the electrodes disappeared at an early stage, and both electrodes remained in apparent equilibrium with the solution up

⁷ Prepared from stock 20% TiCl_3 solution from the Lindsay Light Company. All titanous solutions were kept under hydrogen and all titrations carried out in an atmosphere of carbon dioxide.

to the end-point, where the platinum-rhodium electrode rose above the platinum electrode, the difference decreasing again with increasing concentration of titanous ion. In the titration of ceric sulfate⁸ by titanous sulfate⁹ the platinum-rhodium electrode was slightly more positive up to very near the end-point. It then fell considerably below the potential of the platinum electrode, but as the titration progressed rose rapidly far above it, the difference then decreasing. This is in accordance with the empirical rule mentioned above, since the platinum-rhodium responded less promptly than the platinum to an excess of the reducing agent.

The curves obtained for the titration of iodine with thiosulfate (Fig. 3) show the high reversibility of the electrode potentials in an iodine-iodide mixture. Up to the end-point the electrodes maintain the same potential but in the presence of an excess of thiosulfate a difference immediately appears, in the sense of the rule just referred to.

The titration of hydrogen peroxide with permanganate presents a case in which the electrode reactions are irreversible on both sides of the end-point. The reaction is rather slow in this region and as a result some little time is required for the potentials to reach a constant value. The fact that up to very near the end-point the platinum electrode is the more positive in a decreasing concentration of the reducing agent (hydrogen peroxide) is exceptional, and the only instance of the kind observed in the present work. Just at the end-point the platinum-rhodium is far above the platinum but the relation is reversed again in a comparatively slight excess of permanganate.

The titration of zinc with potassium ferrocyanide was also tested. Although this is a precipitation reaction the precipitant has marked reducing properties and the potential consequently drops sharply at the end-point. Certain peculiarities in the form of this curve have been discussed and explained by Kolthoff¹⁰ and by Treadwell and Chervet.¹¹ With this reaction, however, the potential difference between the electrodes was small throughout and failed to show a sufficiently distinct rise at the end-point to indicate its position satisfactorily.

Experiments with Different Platinum Alloys

The rather characteristic and consistent difference in behavior between the platinum-rhodium electrode and that of pure platinum suggested the

⁸ Prepared from ceric oxide made by the chlorine method. The oxide was dissolved in hydrochloric acid, sulfuric acid added and the solution heated until dense fumes of sulfur trioxide were evolved. The residue was dissolved in water and oxidized electrolytically, using platinum electrodes.

⁹ Prepared by adding concd. sulfuric acid to potassium titanate, heating to complete decomposition of the oxalate and reducing the diluted solution electrolytically, using lead electrodes.

¹⁰ Kolthoff, *Rec. trav. chim.*, **41**, 425 (1922).

¹¹ Treadwell and Chervet, *Helv. chim. acta*, **5**, 633 (1922).

possibility that experiments of this nature might serve as a test of the purity of platinum, or an indication of the impurities present.

Experiments like the one described on pp. 12 and 13, and shown in Fig. 1 were therefore carried out with a number of different alloys, comparing them all with the platinum electrode used in the previous work. All the alloys were in the form of wires except those of platinum-nickel, which were thin, narrow ribbons. In the first experiment (Fig. 4) two platinum-iridium wires, containing about .2% and 10% of iridium, respectively, were employed. Both gave potentials above that of pure platinum in the ferric sulfate solution (containing a trace of ferrous ion)¹² before

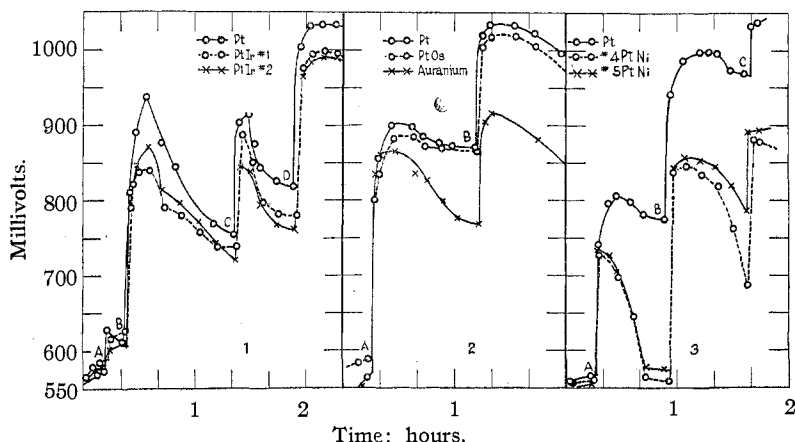


Fig. 4.—Variation of potential with time for various alloys.

Solution, 0.008 M $Fe_2(SO_4)_3$, 0.9 M H_2SO_4 .

Graph 1: at Point A, 0.30 cc. of 0.0002 M $KMnO_4$ was introduced; at Point B, 0.50 cc.; at Point C, 0.20 cc.; at Point D, 1.10 cc.

Graph 2: at Point A, 0.80 cc. of 0.0002 M $KMnO_4$ was introduced; at Point B, 0.50 cc.

Graph 3: at Point A, 0.80 cc. of 0.0002 M $KMnO_4$ was introduced; at Point B, 0.70 cc.; at Point C, 1.10 cc.

any permanganate had been added, but this relation was reversed near the end-point, and thereafter the platinum showed the higher potential. Both alloys showed much the same behavior and the difference in iridium content seemed to have little effect.

In the second experiment, also shown in Fig. 4, the alloys tested were platinum-osmium and "auranum," an alloy of gold and platinum containing about 70% of gold. It is evident that the former gave results very similar to those with platinum-iridium but approached more closely to platinum. The gold alloy, after the first addition of permanganate, fell far below the platinum.

¹² P. 12.

A set of five electrodes loaned by the Western Electric Company was tested in the same way. No. 1 was of platinum of purity probably as high as any yet produced, 2 contained about 0.02% of unknown impurity, probably iridium, 3 contained 0.06% of impurity. Nos. 4 and 5 were platinum-nickel alloys containing 5% and 7½% of nickel, respectively.

Nos. 1, 2 and 3 followed the reference electrode very closely. Their potentials are not given in Fig. 4. The differences were seldom as much as 10 mv. and were too unsystematic to warrant any generalizations concerning the effects of these small amounts of impurities. The nickel alloys, Nos. 4 and 5, gave potentials far below that of pure platinum, as shown in the figure. The difference in nickel content had apparently little effect.

These results may, perhaps, be regarded as throwing some light upon the relative position of the platinum metals with respect to their electro-motive behavior. It is noticeable that osmium and iridium lower the potential of platinum, as do the less noble metals, nickel and gold, while rhodium acts in the opposite direction. As a test of purity, however, the method is disappointing. The effects are distinct only when the impurity is present in considerable amount and would hardly serve to detect small percentages.

The Titration of Silver Ion by Chloride Ion

It is an interesting fact that a freshly ignited platinum or platinum-rhodium electrode will give a sharp drop in potential at the end-point in the titration of silver nitrate with sodium chloride, although this is a reaction in which none of the substances involved has pronounced oxidizing or reducing properties and the hydrogen-ion concentration remains practically unchanged. Our experiments with this phenomenon, however, indicate that it is due, not to gas charges, but to a coating of silver on the platinum. The coating was never visible to the eye and all chemical tests were negative, but its presence was evident from the electrochemical behavior.

It is obvious that if the pretreatment of the electrode has imparted to it a tendency to assume a potential lower than that of silver toward the prevailing silver-ion concentration, the silver ion will tend to deposit upon it until equilibrium is established, after which the electrode will behave like one of pure silver. If, on the other hand, the electrode potential on insertion is above that of pure silver it should remain above and no break would be expected at the end-point. The first case was usually observed when the electrode was simply cleaned with fused potassium bisulfate and ignited in a burner flame before inserting into the silver solution,¹³ and invariably observed when the electrode was dipped into stan-

¹³ This may occur even if the platinum electrode is saturated with air. The calculated potential of the oxygen electrode at 1.0 atm. in a neutral solution is +0.82 volt; the measured potential varies from +0.67 to +0.73 volt. The potential of the air electrode was found by Crotonino [*Z. anorg. Chem.*, **24**, 258 (1900)] to be from 0.1 to 0.15

nous chloride just before use, or when its exposed portion was surrounded with an atmosphere of hydrogen during the titration. The second case could be obtained by charging the electrode electrolytically with oxygen, or by pretreating with a sufficiently strong oxidizing agent. Frequently, however, an ignited electrode behaved in a rather puzzling manner. Its potential increased with the time and after some hours in the stirred solution reached a potential 250 to 300 mv. above the silver potential, thus approaching the potential of an electrode coated with silver sesquioxide,¹⁴ Ag_2O_3 . During the greater part of the rise the effect on the potential of an increase in the silver-ion concentration, or in the acidity, was qualitatively the same as with a pure silver electrode. With further rise the effect varied continuously until actually reversed, thus coming into agreement with what would be expected of a silver peroxide electrode.

It is rather remarkable that even after the rise had carried the potential of the platinum fully 0.1 volt above the silver potential the inert electrode would still serve to indicate the end-point when the silver ion present was titrated with chloride ion, since the break occurred at the proper point and was practically unchanged in magnitude. With further rise, however, the break became smaller and finally almost disappeared.

These facts point to the conclusion that the rise is due to a formation of silver peroxide, but the mechanism of its formation remains unexplained. Precautions to prevent leakage currents in the apparatus were without effect upon the rise, but it was nearly or wholly eliminated by protecting the electrodes with a glass covering at the air-solution interface.

Summary

1. The potential difference between two inert electrodes near the end-point of an oxidimetric titration is primarily a time effect due to a difference in the rate at which the dissimilar electrodes approach equilibrium with a solution of changing composition. This effect is magnified by the enormous increase in the sensitivity of the equilibrium potentials to a given change in concentration near the equivalent point.

2. The end-point as indicated by the abrupt change in the potential difference between the two dissimilar electrodes agrees within the equivalent of 0.05 cc. of 0.1 *N* titrating solution with the end-point as indicated by the single-potential curve for either electrode.

3. With different platinum alloys the relation between time and potential difference depends greatly on the nature of the alloying metal, but the phenomenon is not sufficiently specific to serve as a test for the nature or amount of small percentages of impurity.

volt more negative than the oxygen electrode, that is, between +0.52 and +0.63 volt. The potential of Ag against Ag^+ , 0.1 to 0.01 *M*, lies between +0.74 and +0.68 volt. These values are all referred to the hydrogen electrode as zero.

¹⁴ Luther and Pokorný, *Z. anorg. Chem.*, **57**, 298 (1908).

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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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 article² 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).