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BIMETALLIC ELECTRODE SYSTEMS IN ELECTROMETRIC ANALYSIS. II. THEORY OF BIMETALLIC SYSTEMS: SYSTEMS COMPRISING TWO SIMILAR METALS

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Introduction

It has been shown¹ that the end-point in oxidimetric titrations with bimetallic electrode systems is distinguished by virtue of a difference developed in the electrodes at the end-point and which does not of necessity exist at any other time during the course of the titration. The question remains to be answered as to why there should be any potential difference developed between 2 unattackable electrodes standing side by side in the same solution.

Fredenhagen² in his paper on "The Theory of Oxidation and Reduction Cells" takes up the nearest approach to a discussion of bimetallic systems. He refers the single electrode potential, unattackable-electrode-solution, to gas charges in platinized platinum by simple qualitative experiments which will be taken up later.

Two theories have been advanced for the cause of the existence of a potential between the ions of an oxidizing agent and an unattackable electrode. Le Blanc conceived of an actual interchange of charges between electrode and electrolyte as the cause of the potential difference. Nernst advanced the idea that the potential was due to an oxygen charge, in the case of a reducing agent a hydrogen charge, in the electrode. The former theory requires the conception of a charge without a corresponding ion since the metal is precluded from giving ions to the solution and likewise no deposition of metallic ions is possible. The latter explanation is entirely in agreement with the ionic theory and Faraday's law. According to this view, then, the unattackable electrode functions as a gas electrode. Fredenhagen² developed the Nernst theory further.

Starting with the hypothesis that an unattackable electrode may form a solution with a gas, the expression for the single electrode potential developed, E , may be written

$$\begin{aligned} E &= E_0 + \frac{RT}{(m-n)Q} \ln \frac{(M^{m+})}{(M^{n+})} \\ &= E'_0 + \frac{RT}{2Q} \ln \frac{(H^+)^2}{(H_2)} \\ &= E''_0 + \frac{RT}{4Q} \ln \frac{(O_2)}{(O^-)^2} \end{aligned}$$

where (M^{m+}) and (M^{n+}) represent the ion concentrations of the metal

¹ Willard and Fenwick, *THIS JOURNAL*, **44**, 2514 (1922).

² Fredenhagen, *Z. anorg. Chem.*, **29**, 398 (1902).

M with $m+$ and $n+$ charges; (H^+) , (O^{--}) , (H_2) the other concentrations involved at equilibrium; and E_0 , E'_0 , E''_0 are the respective electrolytic potentials. The other symbols have their usual significance.

It is apparent that a definite hydrogen charge corresponds to a definite oxygen charge and the value of E increases with rising concentration of the hydrogen ion. Since the concentration of the oxygen ion falls off as the hydrogen ion increases, the ratio $(O_2)/(O^{--})^2$ must increase and with it the value of E . The potential of an oxidizing agent is thus increased by the addition of acid. In the case of a reducing agent the potential must obviously decrease under the same conditions. This explains the vast improvement of the break in strong acid solutions. The magnitude of the break depends directly on the difference in the value of E just prior to, and just succeeding, the end-point. The effect of the acid is to increase this difference.

Experimental Support of the Theory

Since the single electrode potential, unattackable-electrode-solution, is determined by the solution pressure of the absorbed gases, it follows that any difference in the functioning of various unattackable electrodes must be due to a difference in their absorbing power for gas.

An electrode which has been freshly ignited and cooled in air, or which has been standing in air for some time, must be saturated with it at practically atmospheric pressure and, therefore, have a definite oxygen charge. Such an electrode if dipped into a solution of ion concentration corresponding to a lower charge must suffer a displacement of absorbed oxygen in order that equilibrium may exist with $(M^{m+})/(M^{n+})$. The concentration of the higher state of oxidation must increase but the actual displacement is extremely small. Fredenhagen calculated the possible oxidation that might be effected by a platinized platinum electrode with a surface of 7.5 sq. cm. saturated with oxygen as equal to 0.0085 cc. of 0.1 N ferrous iron. This is not only entirely negligible for any analytical purpose but is enormously in excess of any oxidation which the much smaller, bright platinum, electrodes used in electrometric work might cause. The ratio $(M^{m+})/(M^{n+})$, therefore, remains practically unchanged, and at equilibrium it is the determining factor in the value of E . This is quite clearly brought out by a determination of the electrode potentials of a number of insoluble electrodes in a solution in which the ratio $(M^{m+})/(M^{n+}) = 1$.

A solution of ferrous sulfate containing 25 cc. of 0.1 N ferrous sulfate and no ferric ion, 20% by volume of conc. sulfuric acid, was exactly $1/2$ oxidized with 0.1 N potassium permanganate solution, and the single electrode potentials of a number of unattackable electrodes were determined. The results are included in the following table.

The same measurements made with a similar solution 50% titrated with 0.1 *N* potassium dichromate also checked with the results above.

TABLE I
SINGLE ELECTRODE POTENTIALS IN A SOLUTION CONTAINING THE SAME CONCENTRATION OF FERROUS AND FERRIC IRON

All the electrodes except tungsten were freshly ignited and cooled in air

Electrode metal	E.m.f. Metal-AgCl Mv.	Electrode metal	E.m.f. Metal-AgCl Mv.
Pt	315	PtIr (2%)	314.5
PtRh	315	PtIr (10%)	313
W	315	PtOs(5%)	314
PtAu	316	Pd (Wire)	314.5
Ir	314.5		

Evidently the difference in the electrodes can be brought out only at the limiting ion concentration or, more comprehensively, when the system is out of equilibrium. When the concentration of either M^{m+} or M^{n+} becomes vanishingly small its osmotic pressure is no longer greatly in excess of the solution pressure of the gas in the electrode. The latter then becomes the governing factor in determining E and a difference in potential immediately develops between 2 electrodes possessing varying solvent power for gas. This potential at limiting concentration has been repeatedly pointed out in connection with ferric-ferrous and permanganate-manganous systems.

In order to demonstrate the dependence of the limiting potential upon the gas charge in the electrode, platinum, platinum-rhodium, and tungsten electrodes were submitted to various methods of pre-treatment and their potentials determined as rapidly as possible in 0.1 *N* solutions of ferrous sulfate and potassium dichromate.

TABLE II
EFFECT OF PRE-TREATMENT ON POTENTIAL OF ELECTRODES

Electrode	Pre-treatment	E.m.f. Electrode-AgCl	
		0.1 <i>N</i> FeSO ₄ Mv.	0.1 <i>N</i> K ₂ Cr ₂ O ₇ Mv.
Pt	H ₂ Cr ₂ O ₇ (cold)	-215 to -359 Av., -277	+955 to +1012 Av., +986
	KOH (hot)	-200 to -309 Av., -277	+333 to +278 Av., +314
Pt	KMnO ₄ (hot)	+203 to +288 Av., +216	+887 to +952 Av., +921
	Ignited	-350 to -365 Av., -360	+357 to +480 Av., +402
Pt	SnCl ₂ + HCl (hot)	0 to -118 Av., -35	0 to -80 Av., -46
	H ₂ SO ₄ (33%, hot)	-9 to -357 Av., -207	+500 to +565 Av., +540

PtRh	H ₂ Cr ₂ O ₇ (cold)	- 20 to -196	+852 to +881
		Av., -115	Av., +863
	KOH (hot)	-300 to +100	+195 to +328
		Av., -60	Av., +268
	KMnO ₄ (hot)	+200 to +218	+710 to +743
		Av., +208	Av., +732
W	Ignited	-330 to -358	+240 to +300
		Av., -346	Av., +272
	SnCl ₂ + HCl (hot)	+ 30 to + 90	- 47 to + 10
		Av., +54	Av., -18
	H ₂ SO ₄ (33% hot)	-250 to + 15	+465 to +515
		Av., -58	Av., +497
PtRh	H ₂ Cr ₂ O ₇ (cold)	0 to +100	+410 to +548
		Av., +50	Av., +469
	KOH (hot)	- 30 to - 49	0 to + 55
		Av., -41	Av., +18
	KMnO ₄ (hot)	+300 to +325	+618 to +746
	(layer MnO ₂ on surface)	Av., +312	Av., +674
	Polished	- 43 to + 16	- 35 to + 35
		Av., -21	Av., -2
	SnCl ₂ + HCl (hot)	-117 to -177	-110 to -135
		Av., -152	Av., -119
	H ₂ SO ₄ (33% hot)	-111 to -141	+ 7 to + 11
		Av., -122	Av., +9

The great variation in potential not only with different pre-treatment but with repeated applications of the same means of enforcing an unbal-

TABLE III
SUMMARY OF EFFECTS OF PRE-TREATMENT

Electrode	0.1 N FeSO ₄	0.1 N K ₂ Cr ₂ O ₇
Pt	Ignited	H ₂ Cr ₂ O ₇
	H ₂ Cr ₂ O ₇	KMnO ₄
	KOH	H ₂ SO ₄
	H ₂ SO ₄	Ignited
	SnCl ₂ + HCl	KOH
	KMnO ₄	SnCl ₂ + HCl
PtRh	Ignited	H ₂ Cr ₂ O ₇
	H ₂ Cr ₂ O ₇	KMnO ₄
	KOH	H ₂ SO ₄
	H ₂ SO ₄	Ignited
	SnCl ₂ + HCl	KOH
	KMnO ₄	SnCl ₂ + HCl
W	SnCl ₂ + HCl	KMnO ₄
	H ₂ SO ₄	H ₂ Cr ₂ O ₇
	KOH	KOH
	Polished	H ₂ SO ₄
	H ₂ Cr ₂ O ₇	Polished
	KMnO ₄	SnCl ₂ + HCl

anced condition is at once apparent. The results at most are only qualitative. No attempt was made to make the time or manner of pre-treat-

ment exactly uniform. In general the electrodes were merely dipped for a few seconds into the various solutions, washed, placed in the reference solution, and the potential quickly read. With cold chromic acid the treatment was extended to about 5 minutes. Platinum and platinum-rhodium were ignited to white heat and cooled in air; tungsten was polished with coarse emery cloth.

When the various methods of pre-treatment are listed in the order of increasing potential with ferrous sulfate and decreasing with potassium dichromate the results are as shown in Table III.

The osmotic pressures of all ions concerned remain the same throughout. There was a large difference in the solution pressures of absorbed oxygen and hydrogen in the electrodes. From the mathematical expressions given it follows that the potential, unattackable-electrode-solution, is directly proportional to the solution pressure of hydrogen in an oxidizing solution and the converse in a reducing solution. In the case of both platinum and platinum-rhodium the results in general bear out this conclusion. The position of sulfuric acid is somewhat anomalous and potassium permanganate decidedly so. With tungsten it will be observed that the order reverses with stannous chloride in hydrochloric acid, chromic acid, and permanganate, indicating that the effect of the pre-treating agent was the same regardless of the reference solution. After treatment with potassium permanganate there was a very thin coat of manganese dioxide visibly adhering to the tungsten surface which was not removed by washing. A partial solution of this when the electrode is placed in the reference solution, provided migration is slow, would result in the potential $\text{MnO}_2 \rightarrow \text{Mn}^{++}$, instead of, unattackable-electrode-solution. The same effect would thus be obtained whatever the surrounding medium. The same explanation may be extended to explain the anomalous position of potassium permanganate with platinum and platinum-rhodium. Very little modification is required to extend the idea to the effect of chromic acid and stannous chloride on tungsten.

Considerable difficulty has been experienced in the past with the inactivation of platinum electrodes used in electrometric work after repeated use in consecutive titrations, particularly with potassium dichromate. Various methods have been suggested for maintaining the electrode efficiency, such as ignition, treatment with chromic acid, ferrous sulfate, or hydrochloric acid. In order to obtain the maximum break at the end-point the condition of the electrode must be as far as possible removed from equilibrium with the solution containing excess of the titrating agent. In oxidimetric reactions, therefore, the hydrogen charge in the electrode should be as high as possible and the oxygen low. If the electrode initially has a high hydrogen charge and the titration is so quickly run that the gas charge just preceding the end-point is in equilib-

rium with a lower potential than the solution, the maximum possible break is obtained. The apparent beneficial effect of oxidizing agents in pre-treating must be due to a cleaning of the electrode surface whereby equilibrium is more quickly established between the electrode and the solution initially, when it is at its strongest reducing power. A rapid titration prevents continuous equilibrium and the break is decidedly better than it would have been if no pre-treatment had been resorted to.

The Effect of Continuous Polarization upon the Electrode Potential

It is evident that any quantitative comparison of the solvent power of different unattackable electrodes for gases must be made when the system is forced out of equilibrium in a more reproducible manner than by any of the pre-treatment methods so far taken up. A polarizing current was selected as the means of accomplishing this.

Suppose the simple case of an insoluble metal immersed in a solution of potassium permanganate. Equilibrium is set up between the solution and the gas charge in the electrode. If, now, this unattackable electrode is connected with a second insoluble electrode in the same solution through a source of current and subjected to an anodic polarization, a higher oxygen charge will be impressed upon it. The actual decomposition of the electrolyte is so slight with low voltage that the osmotic pressure of any ions present is not appreciably altered while the relative change in the solution pressure of the absorbed oxygen is increased considerably, thereby causing an increase in the potential, unattackable-electrode-solution. Upon the nature and degree of the solvent power of the metal for oxygen depends the magnitude of the potential alteration. With a solution of hydrochloric acid and cathodic polarization, the conditions are obviously reversed and a comparison of the effects of absorbed hydrogen is obtainable.

The single electrode potentials of tungsten-platinum and platinum-platinum-rhodium, in identical solutions, were determined. They were then submitted to the effect of a polarizing current of 0.5×10^{-5} amperes for 3 minutes. This was obtained by taking 0.5 volt from a storage battery and interposing a resistance of 100,000 ohms. A very fine platinum wire was used as a polarizing electrode. At the end of this time (the zero second) the relative change in the several potentials was read by the magnitude of the swing of the galvanometer needle on closing the circuit with the comparison electrode. The polarizing circuit was at once broken and the rate at which each electrode returned to its equilibrium potential measured.

The difference in behavior of tungsten from that of the other 2 metals when polarized cathodically is interesting. There is no alteration in the displacement caused by the polarization after the current is broken. This would seem to indicate that the effect here with tungsten is not due to a

solution, pressure of absorbed hydrogen as such but rather to an alteration in the nature of the surface conditions due to oxidation and reduction effects.

TABLE IV
EFFECT OF POLARIZATION

A. Solution pressure of oxygen (Anodic polarization)					
Electrolyte..	0.001 N KMnO ₄				
Polarizing current.....	0.5 × 10 ⁻³ amp.				
Period of polarization.....	3 min.				
Polarizing electrode.....	Pt wire, surface exposure, 3.8 sq. mm.				
Standard electrode.....	0.1 N KCl, AgCl, Ag.				
All readings given as measured, not reduced to absolute values.					
Electrode ^a	Surface exposure Sq. mm.	Initial voltage Mv.	Divisions of galvanometer ^b 0 Sec.	Deflection 10 Sec.	Loss %
Pt	69	+713	+32 to +60 Av., +50	+7 to +17 Av., +10	80
PtRh	49	+687	+32 to +56 Av., +46	+7 to +12 Av., +9	80
W	80	-155	-33 to -47 Av., -38	-7 to -9 Av., -8	79
(Fused) W ^c	270	-142	-17 to -23 Av., -20	-3 to +1 Av., -2	90
(Sintered with 95% ₀ fusing current)					
B. Solution pressure of hydrogen (Cathodic polarization)					
Electrolyte.....	0.001 N HCl				
(Other conditions as under A)					
Electrode	Surface exposure Sq. mm.	Initial voltage Mv.	Divisions of galvanometer 0 Sec.	Deflection 10 Sec.	Loss in 10 Sec. %
Pt	69	+456	-17 to -29 Av., -24	-2 to -4 Av., -3	87.5
PtRh	49	+309	-7 to +8 Av., 0	-3 to +8 Av., +2	
W (Fused)	80	-82	+2 to +13 Av., +6	+2 to +13 Av., +6	0
W (Sintered) ^d	270	-33	+8 to +14 Av., +11	+8 to +13 Av., +11	0

^a The Pt and PtRh electrodes were ignited and cooled in air before polarization. The W electrodes were polished with emery cloth.

^b A + deflection means a swing of the needle to the right, indicating an increase in voltage when E is +.

Although the electrodes showed considerable difference on polarization it seemed advisable to investigate further the effect of current density on these differences before attempting to draw any conclusions, especially since the two forms of tungsten used possessed very different surface exposure, due to the structure of the sintered metal being much less compact than that of the fused. For this purpose the same polarization

experiments were carried out with 3 platinum wire electrodes of various surfaces but all giving the same purity test by the Bureau of Standards thermo-electric method.³ The current density was undeniably not without its effect and conclusions drawn from results obtained with the electrodes of Table IV are not applicable to all electrodes of these same metals without regard to size. As is to be expected the results obtained agreed only roughly. With anodic polarization, in which case the deflections are larger and show up electrode differences, increasing the current density by increasing the impressed current caused a corresponding increase in the magnitude of the polarization, while decreasing the current density by an increase in surface exposure decreased the extent of the displacement. However, an increase in surface of 3600% fell short of cutting the polarization in half so that the effect of the different current densities involved with the electrodes dealt with here will fall within the limits of experimental error and may be omitted from the calculations.

Although the results so far show unmistakable differences in the solution pressures of hydrogen and oxygen in the several electrodes, they offer no suitable basis for the selection of the most satisfactory electrode material. In order to find an expression for this, polarization experiments similar to those given in Table IV were carried out in a solution in which the equivalent concentrations of both an acid and an oxidizing agent were equal; that is, a solution 0.1 *N* with respect to both an oxidizing agent and hydrochloric acid. The results are given in Table V.

TABLE V
EFFECT OF POLARIZATION IN SOLUTIONS CONTAINING EQUIVALENT CONCENTRATION OF
ACID AND OXIDIZING AGENT

Electrode	+ Polarization		- Polarization	
	Initial voltage Mv.	Deflec.	Initial voltage Mv.	Deflec.
Electrolyte, 0.0166 <i>M</i> with respect to $K_2Cr_2O_8$, 0.1 <i>M</i> with respect to HCl				
Pt	+455	+ 41	+470	- 15
PtRh	+438	+ 46	+386	- 7
W	+ 60	+ 52	+ 29	- 2
Electrolyte, 0.0166 <i>M</i> with respect to $KBrO_3$, 0.1 <i>M</i> with respect to HCl				
Pt	+653	+ 23	+495	- 9
PtRh	+520	+ 65	+315	- 3
W	-127	- 24	-141	0
Electrolyte, 0.1066 <i>M</i> with respect to KIO_3 , 0.1 <i>M</i> with respect to HCl				
Pt	+551	+ 93	+535	- 9
PtRh	+521	+109	+491	- 5
W	- 12	- 36	- 3	+ 3

Surface exposure of electrodes: Pt, 69 sq. mm.; PtRh, 49 sq. mm.; W (fused), 160 sq. mm.; Pt polarization electrode, 3.8 sq. mm.

At the completion of an oxidation reaction an electrode ceases to function as a hydrogen electrode and behaves as an oxygen electrode in the

³ Burgess and Sale, "A Study of the Quality of Platinum Ware," *Bur. Standards Sci. Paper*, 254 (1915).

presence of an excess of the oxidizing agent. It is clear from the theoretical discussion which has preceded that the magnitude of the end-point break will be determined by the solution pressure of oxygen and hydrogen dissolved in the electrode. The maximum break will be given with an electrode in which the solution pressure of hydrogen preceding, and oxygen immediately following, the end-point is the greatest possible. If the galvanometer deflections with anodic and cathodic polarization are taken as proportional to the solution pressure of oxygen and hydrogen, respectively, it will be seen at once from Table V that in every case the order of magnitude of the solution pressures in the electrodes investigated was the same, pure platinum being plainly the most desirable, and tungsten the least desirable, electrode metal.

In view of the surprising magnitude of the polarization effects, it seemed possible to utilize a low polarizing current as a continuous means of pretreatment during the course of the titration. Cathodic polarization has the effect of increasing the apparent strength of the oxidizing agent. Either would increase the end-point break. However, in the usual solution titrated the concentration of acid, and consequently of hydrogen ion, is very high. As a result the same impressed currents would have a far greater anodic effect at the end-point, where the opposing osmotic pressure of oxygen ion is very low, than cathodic effect where the osmotic pressure of hydrogen ion is always high. The disappearance of the lower state of oxidation in such high acid concentration causes no appreciable alteration in the osmotic pressure of hydrogen ion.

TABLE VI

EFFECT OF POLARIZATION ON BREAK AT END-POINT WITH MONOMETALLIC SYSTEMS

The solutions titrated contained 25.00 cc. of approximately 0.1 *N* FeSO₄ in an initial volume of 75 cc. Acidity, 33% conc. HCl. Titrating solution, 0.1 *N* K₂Cr₂O₇ 0.1 *N* Soln.

Electrode	Polarization	corresponding to break Cc.	Break Mv.
Pt	None	0.04	47
	Cathodic	0.04	35
	Anodic	0.05	100
PtRh	None	0.04	26
	Cathodic	0.05	23
	Anodic	0.04	111
W	None	} No end-point	
	Cathodic		
	Anodic		

In order to demonstrate this conclusion titrations were run with each of the 3 electrodes previously used with a silver chloride half-cell. First the metallic electrodes were unpolarized, then cathodically, and, finally, anodically polarized. A very small platinum electrode formed the other pole of the polarizing circuit. The current was 0.5×10^{-5}

amperes and was applied during the entire course of the titration. The results are tabulated on preceding page.

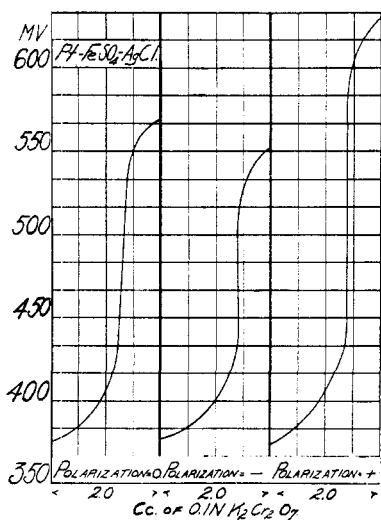


Fig. 1.

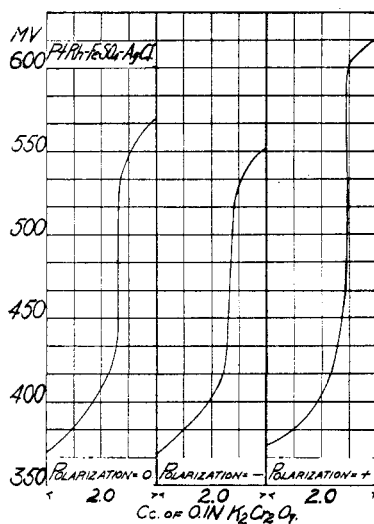


Fig. 2.

Figs. 1, 2, and 3 show graphically the conditions given in Table VI.

Not only is there no increase in the magnitude of the break with negatively polarized platinum and platinum-rhodium electrodes, but there is an actual lessening, due to the apparent weakening of the oxidizing agent. There is no doubt but that positive polarization effects a very material improvement in the break.

With bimetallic combinations of the preceding electrodes, polarization gave even more marked results.

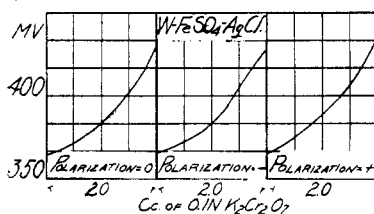


Fig. 3.

TABLE VII

EFFECT OF POLARIZATION ON BIMETALLIC SYSTEMS WITH DISSIMILAR METALS

The solutions titrated contained 25.00 cc. of approximately 0.1 N FeSO_4 in an initial volume of 75 cc. Acidity, 33% by volume of conc. HCl. Titrating solution, 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$

Electrode system	Polarization ^a	0.1 N Soln. corresponding to break Cc.	Average break Mv.
Pt-PtRh	None	0.05	36
	Cathodic	0.05	34
	Anodic	0.05	98
Pt-W	None	0.06	52
	Cathodic	0.05	29
	Anodic	0.06	120

^a Referred to platinum.

In these last experiments no third electrode was used for the polarizing circuit. One of the metallic electrodes was made the positive pole and the other the negative. The results are shown graphically in Figs. 4 and 5.

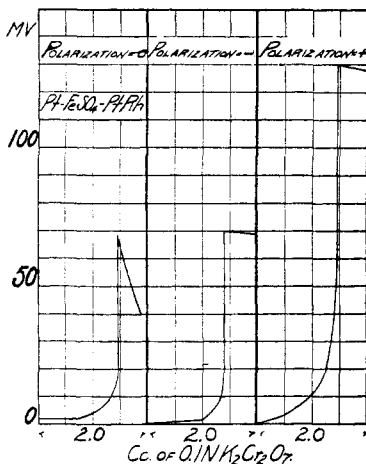


Fig. 4.

Two platinum electrodes were dipped into a solution of ferrous sulfate so that equal areas were exposed, the usual polarizing current was applied, and the solution titrated with 0.1 *N* potassium dichromate. When No. 1 was the anode the break at the end-point was about 190 mv., but when it was the cathode the break dropped below 90 mv. Apparently, this is a much more sensitive test of the relative purity of platinum than the thermo-electric method, for the wires showed no difference in the latter test. With unpolarized wires the system became extremely sluggish in the region of the end-point but gave a discernible break of about 20 mv.

To insure the absolute by identical character of the electrodes No. 1 was cut in two and used for both poles. No end-point was now obtained with unpolarized electrodes, but when polarized the end-point was the sharpest ever obtained with any system and was not affected by a reversal of the impressed current.

Theoretically, at least, since the effect of polarization upon the break with a single metallic electrode depends upon the normal magnitude of that break, the best possible endpoint with a polarized bimetallic system should be obtained with both electrodes of the same metal, and that metal should be the one that normally shows the greatest change as the titration passes through the end-point. Table V showed platinum to be this metal.

Two platinum electrodes were dipped

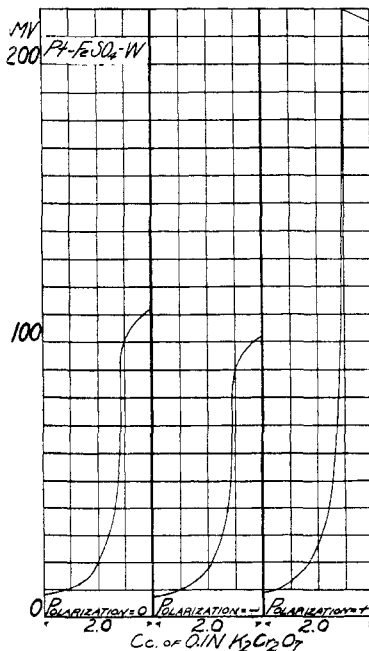


Fig. 5.

TABLE VIII

EFFECT OF POLARIZATION ON BIMETALLIC SYSTEMS WITH SIMILAR METALS

The solution titrated contained 25.00 cc. of approximately 0.1 *N* FeSO₄ in an initial volume of 75 cc. Acidity, 33% HCl. Titrating solution, 0.1 *N* K₂Cr₂O₇

Electrode system	Polarization	Initial voltage ^a		Av. break Mv.
		Polar. Cur. 0 Mv.	Polar. Curr. 0.5 × 10 ⁻⁵ amps. Mv.	
1-2	None			21
	1+	4	42	(Sluggish) 180
	1-	1	42	88
1-1	None	No end-point, sluggish in that region.		
	Right + ^b	0.5	35	216
	Right -	0.5	29	196
W-W (fused)	Right +	No end-point		
	Right -	No end-point		

^a The initial voltages due to polarization fell very rapidly, as always with bimetallic systems, upon the addition of the oxidizing agent.

^b The right-hand electrode was made the anode.

Summary

There seems to be no further evidence necessary to prove that with aqueous solutions of multivalent elements in which the concentration of one state of oxidation approaches either limiting value, the potential, unattackable-electrode-solution, is determined by the magnitude of the solution pressure of gas absorbed by the electrode, and the end-point obtained in oxidimetric titrations with systems comprising 2 unattackable electrodes is given only by virtue of a difference in the solvent power of the 2 metals for gas. When the concentration of oxygen ion, or hydrogen ion, becomes vanishingly small, the osmotic pressure is too low for a saturation of the electrodes with the corresponding gas. The 2 elements receive the charge in accordance with the distribution law, and a difference in potential develops which is at its maximum with minimum concentration of the corresponding ion and which falls rapidly as this ion concentration rises to a value in excess of that required for the saturation of both electrodes.

The proposed bimetallic system⁴ provides a type of electrode system essentially different from those previously adopted.⁵ A comparison of

⁴ This is not the first system to make use of polarization effects. Dutoit and v. Weisse, *J. chim. phys.*, **9**, 578 (1911), used a polarized platinum electrode with the regular system, [p. 2504 (1)] for a number of precipitation reactions. A second platinum electrode formed the other pole of the polarizing circuit and the applied e.m.f. was greater than that used in the work described here. A calculable amount of the metal under investigation was deposited upon the electrode during the course of the titration. The results obtained were not, on the whole, satisfactory.

Merriam, "The Theory of the Residual Current," (*Dissertation*, Göttingen, 1906), used a polarized system for neutralization reactions. A stream of hydrogen was conducted through the solution during the titration.

the relative values of the regular monometallic and bimetallic systems may be based upon the difference in the mechanics of the end-point in the two cases. The change in voltage with the former, which is a true oxidation potential, is continuous throughout and rises to a maximum at the end-point. With the latter practically all change is confined to within less than 0.5 cc. of the completion of the titration. Although the actual

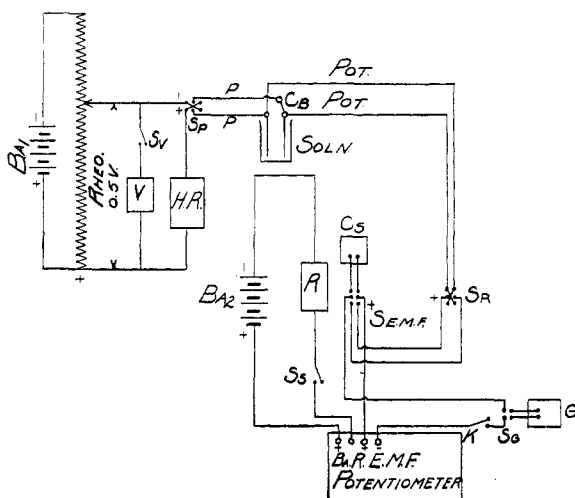


Fig. 6.

Key to Fig. 6.

BA ₁ , Storage battery for polarizing.	POT.-POT., Leads from electrodes to potentiometer system.
BA ₂ , Edison storage battery.	Soln., Beaker containing solution to be titrated.
RHEO., Rheostat for taking off polarizing voltage. About 0.5 volt used.	S _r , Reversing switch.
V, Voltmeter.	S _{e.m.f.} , Switch for throwing in standard cell or solution to be titrated.
Sv, Voltmeter switch.	C _s , Standard cell.
H.R., High resistance, 100,000 ohms.	R, Setting resistance for potentiometer.
Sp, Reversing switch for polarizing circuit.	S _a , Battery switch.
P, P, Polarizing leads to electrodes.	S _g , Galvanometer switch.
C, Mercury cup commutator.	G, Galvanometer.
B, Removable bridge in case monometallic systems is desired.	K, Tapping key.

The potentiometer was a "students'" potentiometer. This instrument was found satisfactory for all purposes. It may be operated rapidly and its accuracy is entirely sufficient. The galvanometer was the ordinary lamp-and-scale box-type. A potential difference of 1 mv. through the potentiometer circuit caused a deflection of 10 scale divisions.

⁵ Willard and Fenwick, This Journal, **44**, 2504 (1922).

On account of the convenience of its buret and beaker supports, a Kelley electro-metric titration apparatus was partially remodeled for use here. The electrode connections were removed, since no use was made of the potentiometer system, and the entire calomel electrode arrangement discarded. A small 3-cup mercury commutator, C in the diagram, was mounted on the reservoir support. By removing the wire bridge, B, the polarizing circuit was broken and only the regular potentiometer system remained.

The polarizing circuit is self-explanatory. There is no necessity that the high resistance interposed be accurate. A carbon resistance answers the purpose very well.

The particular electrode combination used in any case is described in the discussion of the given titration. For most of the work two identical platinum electrodes were used. In the early part of the investigation a special platinum was used almost entirely but later "C.P." platinum thermocouple wire was obtained in several sizes which was perfectly satisfactory. Usually, the wires were securely attached to short pieces of B. and S. No. 8 copper wire by winding tightly with fine copper wire, slipped through small rubber stoppers, and inserted in the electrode supports of the Kelley apparatus. The heavy copper wire provided a firm support for screw connections and saved wear and tear on the fragile platinum. When it was found necessary to use short pieces of wire they were sealed into Pyrex tubing and connections made with the lead wires by filling the tubes with mercury.

magnitude of the break is normally less than with monometallic combinations, it is, relative to the preceding rise, much greater, hence the sharpness of the end-point is correspondingly increased, insuring greater speed and accuracy. With the use of polarized bimetallic systems the break may be increased so much as to leave no possible comparison favorable to the monometallic system. It is thus possible to titrate solutions which offer too small potential differences between two possible states of oxidation for a good end-point with the regular apparatus.

The polarizing circuit may be made so integral a part of the usual apparatus that it requires no attention and presents no difficulties.⁶ Uniform results are insured, there is no possible inactivation of the electrodes, no stopping for electrode pre-treatment of any kind, none of the inherent bother of the standard half-cell.

As for the disadvantages of the new system, the greater localization of the total potential change makes it more difficult to anticipate the end-point as readily as with the other apparatus. Enough warning is given, however, to make the danger of over-titration negligible after a very little practice. Obviously, from the equations for the electrode potential, the velocity of the titration reaction must be infinitely great in comparison with the velocity of the back diffusion of the absorbed gas in the 2 metal electrodes. This prerequisite makes the question of reaction velocities of greater importance than with the monometallic system and renders the latter more desirable for certain titrations.

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⁶ The apparatus used in all work described here is shown diagrammatically in Fig. 6.