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The Rest Potentials of Platinum, Rhodium and Iridium Electrodes

by

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The Rest Potentials of Platinum, Rhodium and Iridium Electrodes

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The reduced and oxidized platinum, rhodium and iridium electrodes were alternately dipped, as, cathode into the solutions of 1 N H_2SO_4, 1 N HNO_3, 1 N H_2SO_4 + 1/8 M $K_2Cr_2O_7$, 1 N HNO_3 +1/8 M $K_2Cr_2O_7$, 1/4 M CrO_3, 1 N H_2SO_4 + 10^{-2} M Ce (IV) SO_4, 1 N NaOH, 1 N NaOH + 1/8 M $K_2Cr_2O_7$. The potentials with respect to time were measured against a calomel electrode, (rest potentials). The electrodes were pretreated in two separate ways.

The electrode, as anode, was dipped into a 1 N solution of H_2SO_4. A current of 200 mA was passed for a period of five minutes.Then the oxidized electrode was again dipped into a same type solution with continuous flow of nitrogen while being connected to a calomel electrode in short circuit (reduced electrode).

The electrodes prepared according to the above procedure were again oxidized, anodically, for fifteen minutes under a current of 200 mA (oxidized electrodes).

Using the same electrolyte, the rest potentials for platinum, rhodium and iridium were found to have different values. The rest potentials for these metals in the solutions mentioned above were very close to the equilibrium potentials of the same metals in the oxidized state this indicates. That they were being oxidized in these solutions.The time required for such metals to reach equilibrium was shortest for iridium next for rhodium and platinum.

INTRODUCTION

The fact that the reduction of bichromate on platinum, gold and palladium electrodes occurs on the same reduction potentials of their oxides, was previously indicated by one of us [1]. Both the previous study and the present work verifies that the electrodes are oxidized and coated with a film of oxide when they are inserted in bichromate solutions.

In this study, rest potentials in various oxidizing systems have been determined to investigate whether noble metals such as platinum, rhodium and iridium are oxidized in oxidizing media.

EXPERIMENTAL

In this series experiment great care was taken to see that all chemicals were chemically pure and solutions were prepared with conductance water and the glass ware was made of pyrex glass. The cell used to determine the rest potentials was a three armed one. The first arm was the anode; the second arm was the cathode compartment. The reference calomel electrode was dipped within the third arm. The stopcock between the second and the third arm was kept close in order to prevent the diffusion of chloride ions.

Variations of cathode potentials with time, in various oxidizing solutions were measured against a saturated calomel electrode and apparatus used to determine the potential was Knickmessverstärker (Berlin).

The solution in the cell was kept at the same level and mixed continuously with a magnetic stirrer during experiment. The electrodes used as cathodes were platinum, rhodium and iridium wires in 3 cm lenght and 0.5 mm diameter.

As many investigators [1-6] have indicated current - potential and potential - time curves change in accordance with the pretreatment of the electrodes. Therefore to get reproducible curves electrodes were subjected to the same procedure [2-1], before experiment.

Reducing the electrodes: The electrode was dipped into 1 N H_2SO_4 solution as anode and a current of 200 mA was passed for five minutes. Then the oxidized electrode was dipped in a cell which contain 1 N H_2SO_4 solution through which nitrogen gas was passed continuously and the electrode was connected to a calomel electrode in short circuit. The potential of electrode, reduced against calomel was measured with a potentiometer at intervals and the reduction procedure ended 400 - 350 mV for platinum and 280 mV for rhodium and iridium. These values are given as

potentials for this metals when oxide layer produced with anodic polarization had just been removed but hydrogen adsorption had not yet began [6]. In this text the electrodes prepared in the above manner are called "reduced electrodes".

Oxidizing the electrodes: The reduced electrodes prepared with the above procedure were again oxidized, anodically, for fifteen minutes under a current of 200 mA. These electrodes are called "oxidized electrodes".

The rest potentials curves have been obtained both with oxidized and reduced electrodes.

CONCLUSIONS

As may be observed in figure 1, 2, 3 and 4 the curves of oxidized and reduced electrodes reached the same potentials value in a certain period. In figure 1 the rest potentials curves of platinum, rhodium and iridium electrodes in 1 N H_2SO_4 are shown. An oxidized platinum electrode when dipped in 1 N H_2SO_4, a potential around 1280 mV is observed, however, this potential drops until 920 mV and remained fixed thereafter. Moreover a reduced platinum electrode showed a potential of 900 mV when dipped in the same solution at the beginning. Then it roses speadily to 940 mV which is the maximum point and remained fixed around 900 mV.

The curve obtained with oxidized rhodium electrode has shown an inflection point at 1060 mV and dropped to a constant value of 770 mV. The curve obtained with reduced rhodium electrode showed a maximum of 880 mV and potential decreased slowly to 770 mV and was stable at this value. The curve of oxidized and reduced iridium electrodes reached to the same constant value (810 mV). The curve of reduced iridium electrode reaches to the maximum point at 855 mV.

Hoare [7-9] measured the potential of platinum, rhodium and iridium electrodes after oxidizing them anodically in 2 N H_2SO_4 saturated with oxygen and then measured their potentials in the same solutions. The results of this study found to be in good agreement with those of Hoare's. Bianchi and Mussini [3] found 960 mV for

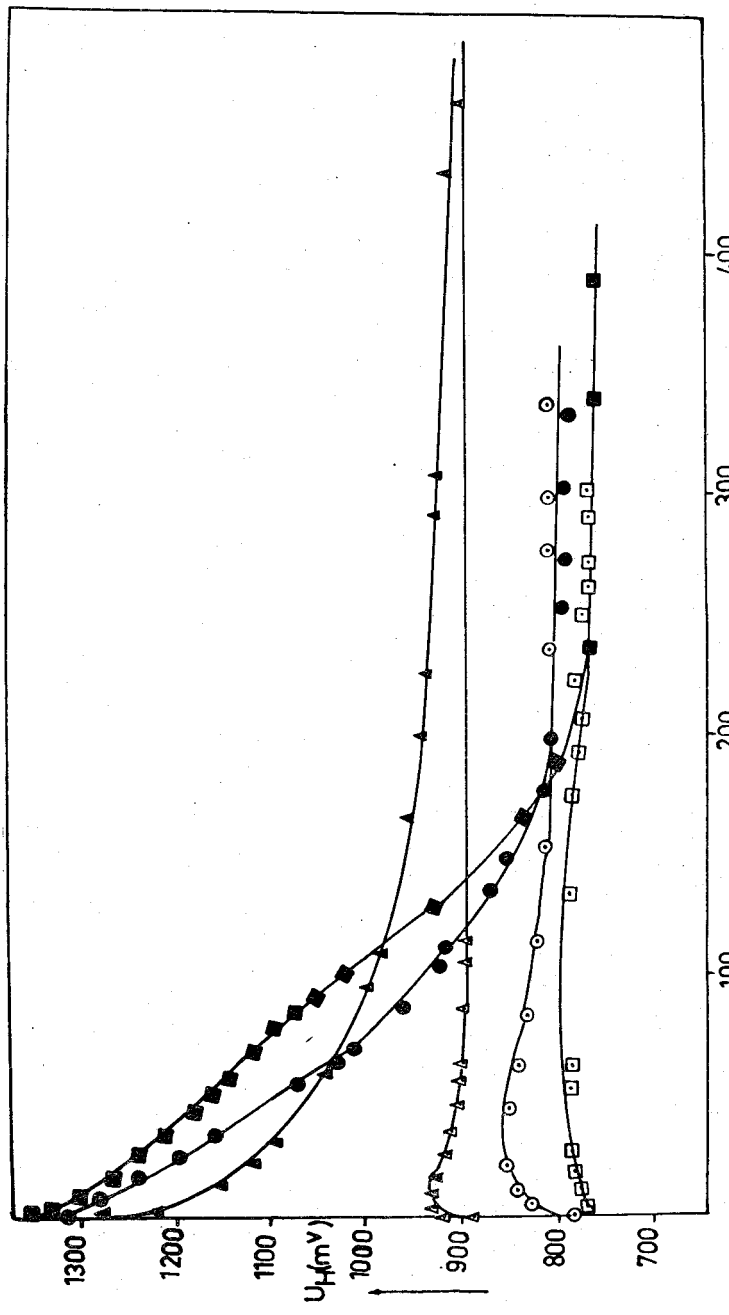

Fig. 1. The rest potentials of platinum, rhodium and iridium in 1 N H_2SO_4 solution. Open figures for reduced electrodes, filled figures for oxidized etectrodes. ■ □ rhodium, ● ○ iridium, ◆ ◇ platinum

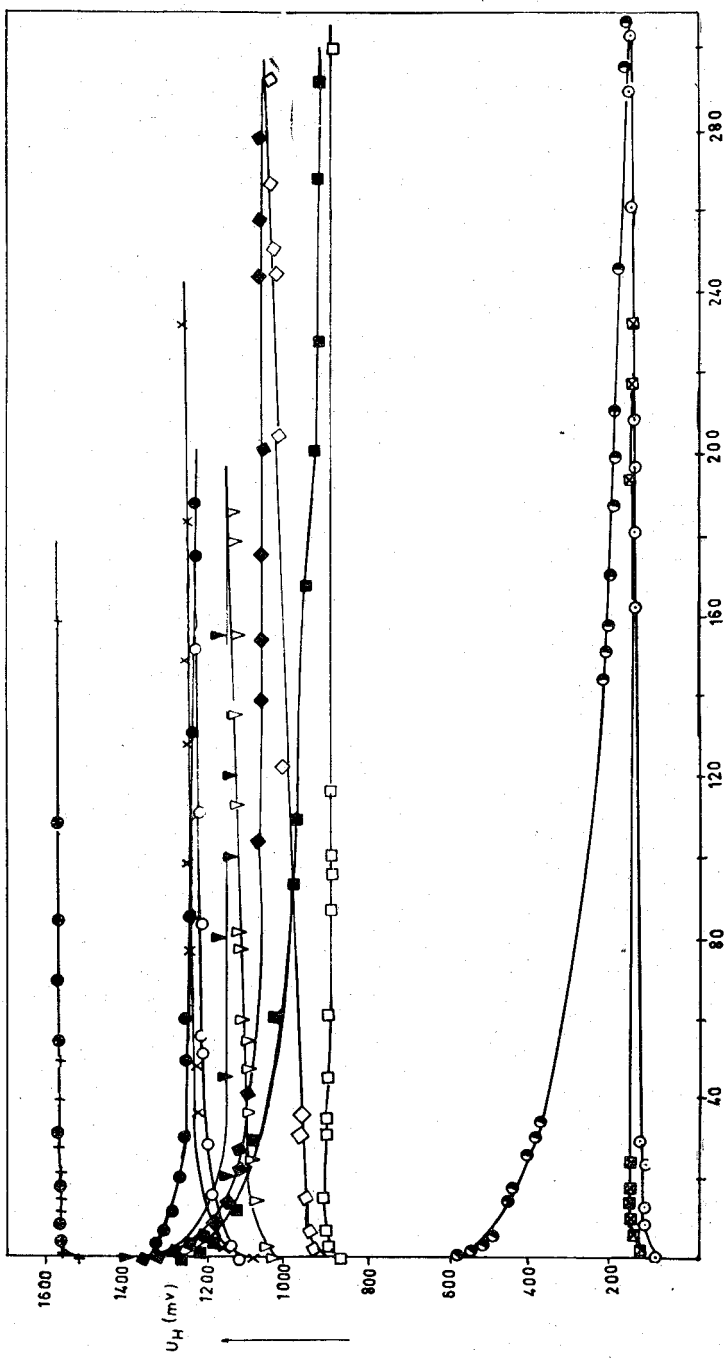

Fig. 2. The rest potentials of platinum electrode in various oxidizing media. Open figures for reduced electrode, filled figures for oxidized electrode ⊕ $+1NH_2SO_4 + 10^{-2}$ M Ce (IV)SO_4, X 1/8 M $K_2Cr_2O_7$ + 1 N HNO_3, ● ⊙ 1/8 M $K_2Cr_2O_7$ + 1 N H_2SO_4, ▼ ▽ 1/4 $MCrO_3$, ◆ ◇ 1 N HNO_3, ■ ⊡ 1 NH_2SO_4 ◔ ○ 1 N NaOH, |⊟| 1 N NaOH + 1/8 M $K_2Cr_2O_7$

the rest potential of platinum electrode in 0.5 N H_2SO_4. In figures. 1, 2, 3 and 4 the potential - time curves for oxidized and reduced platinum, rhodium and iridium electrodes in various solutions are shown. The equilibrium values obtained from these curves are presented in table I. In table II the theoretical values calculated by Latimer and the experimental values measured by Hoare are given.

DISCUSSION

As it is seen in figure 1, 2, 3, 4 and table I these three metals have different rest potentials in the same solutions. The rest potentials in acidic media are different from the normal potentials of O_2/H_2O system but these potentials are almost equal to normal potentials of electrode metal oxides given by Latimer and Hoare.

The fact that various curves in figures get fixed at certain potentials levels are equal to various metal oxides can well be understood when these potentials levels are compared with the table II. That is, there is an agreement between the maximum, noticed in the curve obtained in 1 N H_2SO_4 with the reduced rhodium electrode and the normal potential of reaction 3 determined by Hoare at table II. Similarly, there is an agreement between the maximum around 855 mV seen at the curve of reduced iridium electrode in 1 N H_2SO_4 and the normal potential of reaction 5 determined by Hoare. The rest potential found for platinum electrode in 1 N HNO_3 and the normal potential of the reaction 4 of the Latimer indicated at table II are almost the same. Oxidized rhodium electrode curve which is obtained in 1 N H_2SO_4 has an inflection point at 1060 mV. The rest potential of rhodium electrode in 1 N HNO_3 is almost the same with the above value, (1050 mV). Moreover rest potentials obtained in 1 N NaOH have shown that electrodes can be oxidized in basic media as well as in acidic media. The values of 170 mV and 140 mV for platinum and iridium respectively are close to the potentials of reactions 1 (for platinum) 2 or 3 (for iridium) in table II. For this metals the time required to reach equilibrium decreases the order of "thermodynamic nobility" in accordance with. For rhodium and iridium (Fig. 3, 4) the rest potentials obtained between 1600 and 800 mV in various

oxidizing media are cumulated in definite potential regions, but the curves of platinum (fig 2) are dispersed between above values. This can be explained by the fact that definite oxides are formed on the surface of rhodium and iridium electrodes in accordance with the oxidizing power of the solution. But in the case of platinum, mixed oxides are formed on the electrode surface. Anson and Lingane[10]had shown that the oxide film formed on the surface of platinum by anodic polarization or by different oxidizing agents were mixtures of PtO_2 and real PtO.

The rest potentials obtained with these electrodes in bichromate solutions are different from each other as in the case of Ce (IV) SO_4 + 1 N H_2SO_4 and have different values according to the kind of acid present in the medium. According to Müller[11] and Knorr[12]the surface of the electrode is coated with a film of chromil chromate as soon as it is inserted into a chromic acid solution. If this assumption is right, the rest potentials in chromic acid solution should be the same for both of the three electrodes. If the surface of these metals are not oxidized by bichromate or chromic acid, the phenomena would be the same (the formation of chromil chromate) and therefore the rest potentials would be the same.

TABLE I

The rest potentials of platinum, rhodium and iridium electrodes in various oxidizing media

Medium	Platinum (mV)	Rhodium (mV)	Iridium (mV)
1 N H_2SO_4 + 10^{-2} M Ce(IV) SO_4	1575	1555	1525
1/8 M $K_2Cr_2O_7$ + 1 N HNO_3	1255	1275	1290
1/8 M $K_2Cr_2O_7$ + 1 N H_2SO_4	1240	1250	1275
1/4 M CrO_3	1160	1200	1240
1 N HNO_3	1075	1050	1070
1 N H_2SO_4	900	770	800
1 N NaOH	170	140	140
1 N NaOH + 1/8 M $K_2Cr_2O_7$	160	110	120

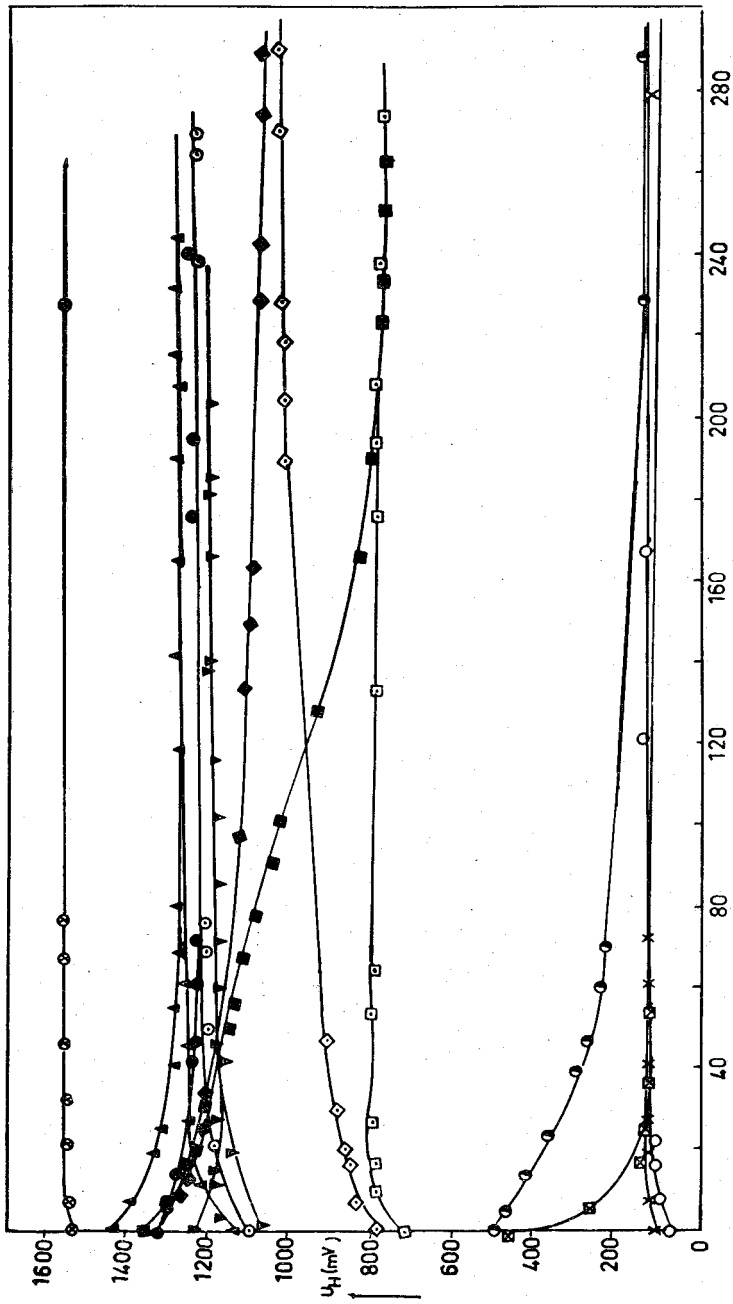

Fig. 3. The rest potentials of rhodium electrode in various oxidizing media. Open figures for reduced electrode, filled figures for oxidized electrode
⊗ 1 N H_2SO_4+10^{-2} M Ce(IV)SO_4, ▲ △ 1/8 M $K_2Cr_2O_7$+ 1 N HNO_3, ● ○ 1/8 M $K_2Cr_2O_7$+1 N H_2SO_4, ▼ ▽ 1/4 M CrO_3, ◆ ◇ 1 N HNO_3, ■ □ 1 N H_2SO_4 ◑ ○ 1 NNaOH, ⊞ X 1N NaOH+ 1/8 M $K_2Cr_2O_7$

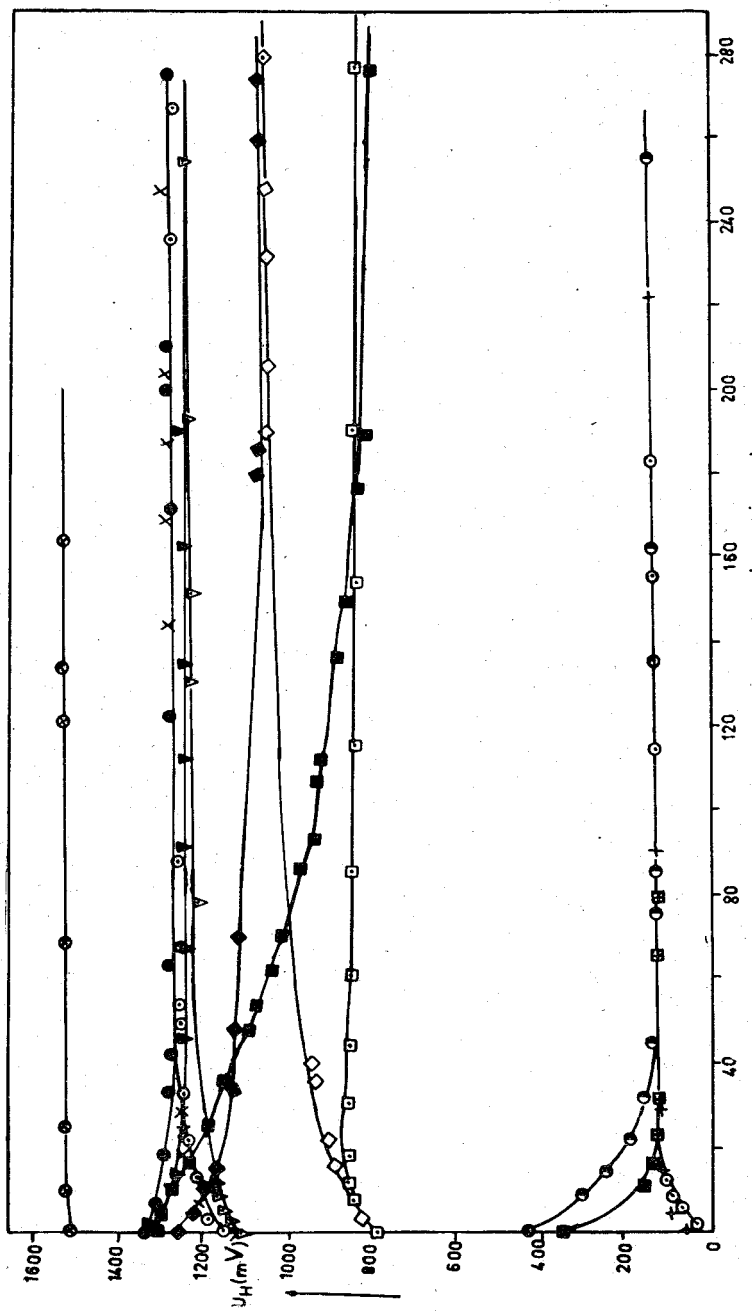

Fig. 4. The rest potentials of iridium electrodes in various oxidizing media. Open figures for reduced electrode, filled figures for oxidized electrode
⊗ 1 N H_2SO_4 + 10^{-2} M Ce (IV)SO_4, X 1/8 M $K_2Cr_2O_7$ + 1 N HNO_3, ● ⊙ 1/8 M $K_2Cr_2O_7$ + 1 N H_2SO_4, ▼ ▽ 1/4 $MCrO_3$, ◆ ◇ 1 N HNO_3, ■ □ 1 N H_2SO_4, ◑ ⊙ 1 N NaOH, ⊟ + 1 N NaOH + 1/8 M $K_2Cr_2O_7$

TABLE II

Electrode (metal)	Latimer's calculated values: Reactions	$E°_B$(V)	Hoare's experimental values: Reactions	potentials (mV)
Platinum	1. $2OH^- + Pt = Pt(OH)_2 + 2e$	− 0.150	1. $PtO + 2H^+ + 2e \rightleftarrows Pt + H_2O$	880
	2. $Pt + 2H_2O = Pt(OH)_2 + 2H^+ + 2e$	− 0.980		
	3. $Pt(OH)_2 + 4OH^- = Pt(OH)_6^= + 2e$	− 0.1 to − 0.4		
	4. $Pt(OH)_2 = PtO_2 + 2H^+ + 2e$	− 1.100		
Rhodium	1. $2Rh + 3H_2O = Rh_2O_3 + 6H^+ + 6e$	− 0.870	2. $Rh_2O_3 + 6H^+ + 6e \rightleftarrows Rh + 3H_2O$	880 ∓ 10
	2. $2Rh + H_2O = Rh_2O + 2H^+ + 2e$	− 0.950	3. $RhO + 2H^+ + 2e \rightleftarrows Rh + H_2O$	810 ∓ 15
	3. $4OH^- + RhO_2 = RhO_4^= + 2e + 2H_2O$	> − 0.90		
	4. $2OH^- + Rh_2O_3 = 2RhO_2 + H_2O + 2e$	> − 0.90		
Iridium	1. $Ir + 2H_2O = IrO_2 + 4H^+ + 4e$	− 0.930	4. $IrO_2 + 4H^+ + 4e \rightleftarrows Ir + 2H_2O$	935 ∓ 5
	2. $Ir + 4OH^- = IrO_2 + 2H_2O + 4e$	− 0.100	5. $IrO + 2H^+ + 2e \rightleftarrows Ir + H_2O$	870 ∓ 20
	3. $Ir + 6OH^- = Ir_2O_3 + 3H_2O + 6e$	− 0.100		
	4. $IrO_2 + 4OH^- = IrO_4^= + 2H_2O + 2e$	− 0.400		

REFERENCES

[1.] S. Üneri, Communication de la Faculte des Sciences de L'universite D'Ankara, serie: B Chim., Tome X, 7 (1962)

[2.] I. M. Kolthoff and A. M. Shams El Din, J. Phys. Chem, **60**, 1564 (1956)

[3.] G. Bianchi and T. Mussuni, Electrochim. Acta, **10**, 445 (1965)

[4.] R. Weiner, Zeit, für Elec. Chem., **42**, 377 (1936)

[5.] R. Weiner, E. Ney and C. Schile, Metalloberfläche, **14**, 69 (1960)

[6.] F. G. Will and C. A. Knorr, Zeit. für Elec. Chem., **64**, 271 (1960)

[7.] J. P.Hoare J. Elec. Chem. Soc., **109**, 858 (1962)

[8.] " " " " **111**, 232 (1964)

9.] " " " " **110**, 987 (1964)

[10.] Fred Anson and J. Lingane, J. Amer. Chem. Soc., **79**, 4901 (1957)

[11.] Müller and O. Essin, Zeit. für. Elec. Chem., **36**, 2 (1930)

[12.] D. Reinkowski and C. A. Knorr, Zeit. für Elec. Chem., **63**, 59 (1959)

ÖZET

Oksitli ve redüklenmiş platin, rodyum ve iridyum elektrotlar 1 N H_2SO_4, 1 N HNO_3, 1 N H_2SO_4 + 1/8 M $K_2Cr_2O_7$, 1 N HNO_3 + 1/8 M $K_2Cr_2O_7$, 1/4 M CrO_3, 1 N H_2SO_4 + 10^{-2} M Ce (IV) SO_4, 1 N NaOH, 1 N NaOH+1/8 M $K_2Cr_2O_7$ çözeltileri içine daldırılarak, potansiyelleri doygun kalomel elektroda karşı izlenmiştir, (sükunet potansiyeli).

Elektrotlar iki türlü ön muameleye tâbi tutulmuştur.

1. 1 N H_2SO_4 içinde 5 dakika 200 mA de oksitlenen elektrotlar, içinden azot gazı geçirilen 1 N H_2SO_4 içine daldırılarak kalomel elektroda karşı kısa devre yapılmıştır, (redüklenmiş elektrot).

2. Yukarıdaki yolla redüklenen elektrotlar tekrar 15 dakika 200 mA de oksitlenmiştir, (oksitli elektrot).

Aynı bir çözelti içinde platin, rodyum ve iridyum elektrotların sükunet potansiyellerinin birbirinden farklı olduğu tesbit edilmiştir. Yukarıdaki muhtelif çözeltiler içinde her üç elektrotla elde edilen sükunet potansiyellerinin literatürde bu metallerin oksitleri için verilen denge potansiyellerine yakın olması, muhtelif yükseltgenlerin asil metallerin yüzeyini oksitlediğini göstermektedir.

Denge değerine en kısa zamanda ulaşan iridyumdur, onu sıra ile rodyum ve platin izlemektedir, (Termodinamik soyluk sırası).

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