

OXIDATION POTENTIALS FOR SOME TRANSITION ELEMENTS

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Introduction

This report consists of a tabulation of standard oxidation potentials for several of the transition elements, all referring to aqueous solutions at 25°C. Many of these values are derived from more recent data than were considered in earlier compilations of thermodynamic data¹ and oxidation potentials². Sources of data cited here are not listed in this report, but will be listed in detail, along with related thermodynamic data, in subsequent publications. Readers who are interested in this detailed discussion of sources of these potentials and in the related thermodynamic data may obtain some of these before further publication by communicating with the author. Some further potentials will also be tabulated later.

In spite of considerable discussion³⁻⁶ in recent years, general agreement is still lacking on "sign conventions" for potentials. Much of the confusion arises because "sign" can be either electrical or algebraic.

Potentials measured in the laboratory are positive or negative in an electrical sense. These electrical cell potentials lead to electrode potentials (based on an arbitrary conventional value for a reference electrode) that are also positive or negative in an electrical sense. The electrical signs of these electrode potentials are independent of how we write the electrode reactions. The standard electrode potential of a Ag/Ag^+ electrode (taking $E^0 = 0.0$ v for the H_2/H^+ electrode) is conveniently

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represented as $\oplus 0.8 \text{ v}$ where $\oplus$ is written to emphasize that the sign is electrical and is independent of how we choose to represent the electrode or the reaction that occurs at the electrode.

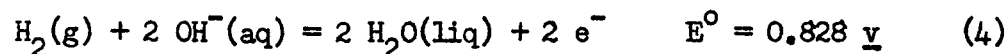
On the other hand, the potentials that are used in thermodynamic calculations are positive or negative in an algebraic sense. We may call these quantities reaction potentials and half reaction potentials to distinguish them from cell potentials and electrode potentials that have electrical signs. The algebraic signs of these reaction potentials and half reaction potentials depend on the directions of the reaction or half reaction equations under consideration. Thus we write



and



The potential in (1) may be called an (algebraic) oxidation potential for the Ag/Ag^+ half reaction while the potential in (2) is an (algebraic) reduction potential for the Ag^+/Ag half reaction. All potentials tabulated in this report are oxidation half reaction potentials with algebraic signs as in (1). These tabulated half reaction oxidation potentials are based on the usual references:



The standard states relevant to these standard potentials are also the usual ones^{1,2}.

It might be mentioned that the decision to tabulate half reaction potentials with algebraic signs rather than electrode potentials with

electrical signs (+ is not necessarily interchangeable with $\oplus$) was based on a greater personal interest in thermodynamics and chemical equilibrium than in electrochemistry. It may be that future tabulations should be made in terms of reduction potentials so that + and $\oplus$ are equivalent and - and $\ominus$ are equivalent, thus eliminating the need to think about the meaning of "sign".

The "sign convention" used here permits straightforward use of the familiar $\Delta G^\circ = -nFE^\circ$, which at 25°C is conveniently transformed to

$$\log K = 16.9 n E^\circ \quad (5)$$

In addition to giving oxidation potentials, Latimer's practice² of also presenting these same data in the form of potential diagrams has also been followed.

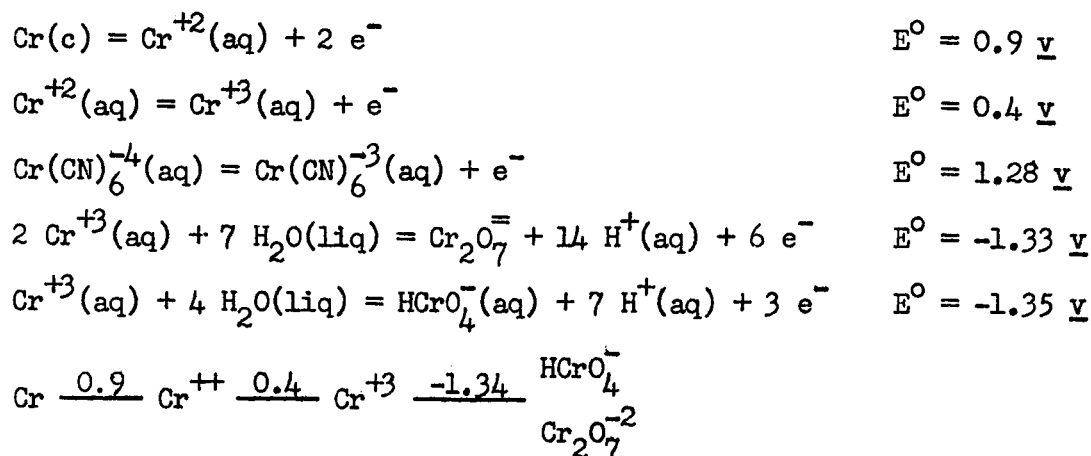
Many of the potentials tabulated in this report were obtained from electrochemical measurements. Many others were obtained from thermodynamic data. These approaches have been summarized authoritatively⁷ and also in more elementary fashion⁸.

For some compounds and ions of interest, we are lacking standard potentials, but we do have data that refer to a particular concentration of some particular electrolyte. In reporting such potentials, the superscript ^o is omitted and the medium is described in parentheses. For example, a potential that applies to 1 M KCl is indicated by E(1 M KCl). Most of the available data apply at 25° -- all others are specifically indicated as by E(20°).

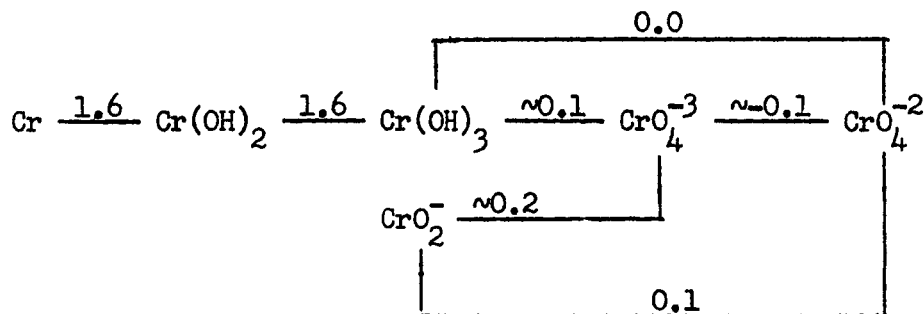
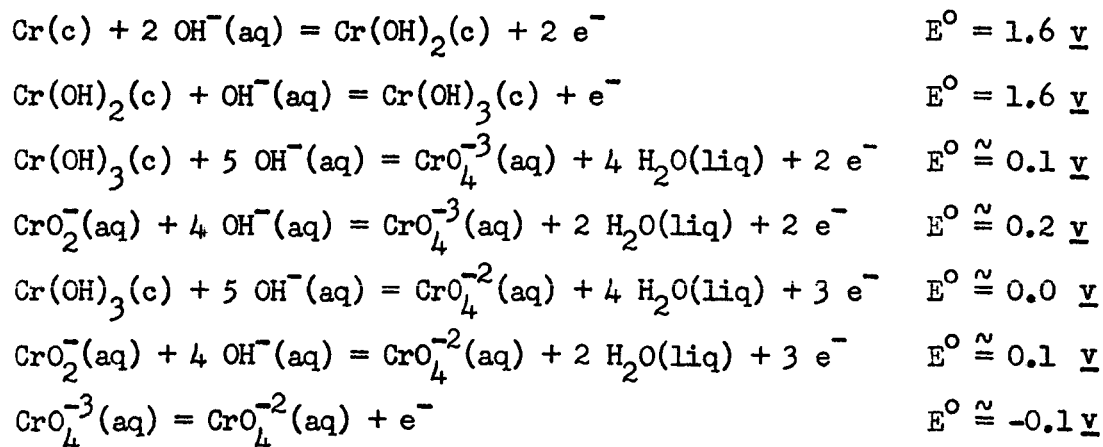
Estimated potentials are all enclosed in parentheses, as $E^\circ = (0.5) \text{ v.}$ In some cases we have potentials that lead to "experimental" standard potentials that are quite uncertain for any of a variety of reasons. Such approximate potentials are indicated by $\approx$.

Chromium

Acidic solution:

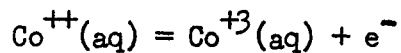


Basic solution:



$$\text{Co(c)} = \text{Co}^{++}(\text{aq}) + 2 \text{e}^{-}$$

$$E^{\circ} = 0.29 \text{ v}$$



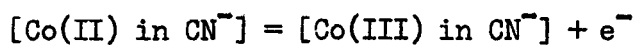
$$E(1 \text{ N } \text{H}_2\text{SO}_4) = -1.81 \text{ v}$$

$$E(4 \text{ M HClO}_4) = -1.95 \text{ v}$$

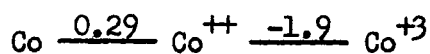
$$E(3 \text{ M HNO}_3) = -1.84 \text{ V}$$

$$E(4 \text{ M HNO}_3) = -1.85 \text{ V}$$

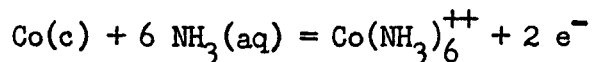
$$E^{\circ} \approx -1.9 \text{ v}$$



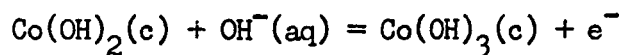
$$E^{\circ} = (-1.0)$$


$$\text{Co(c)} + 2 \text{OH}^-(\text{aq}) = \text{Co(OH)}_2(\text{c}) + 2 \text{e}^-$$

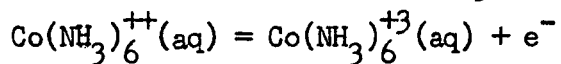
$$E^{\circ} = 0.77 \text{ v}$$



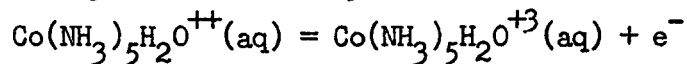
$$E^{\circ} = 0.43 \text{ v}$$



$$E^0 = -0.26 \text{ v}$$

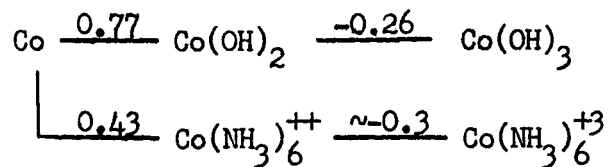


$$E^0_{H_2} = -0.3 \text{ V}$$



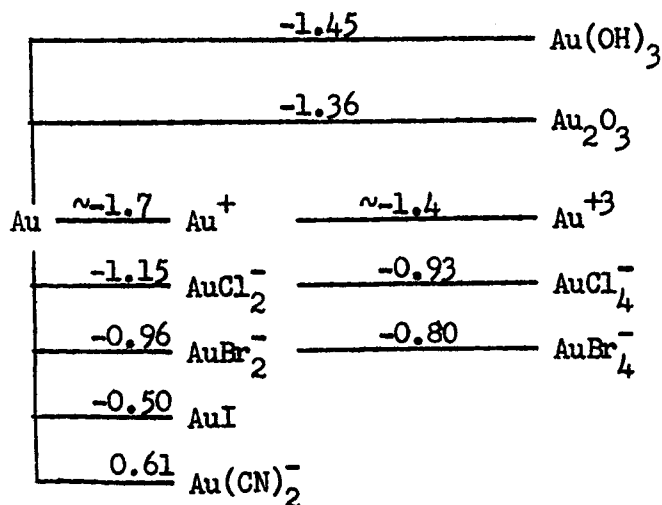
$$E(1 \text{ M } \text{NH}_4\text{NO}_3) = -0.37 \text{ v}$$

$$E(1 \text{ M } \text{NH}_4\text{ClO}_4) = -0.33 \text{ v}$$



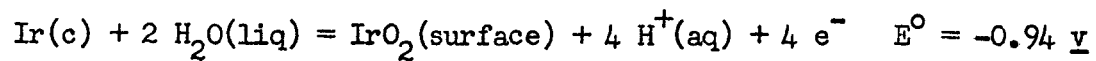
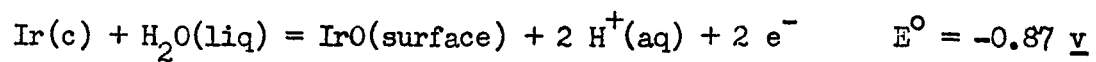
Gold

$\text{Au(c)} + 2 \text{Cl}^-(\text{aq}) = \text{AuCl}_2^-(\text{aq}) + \text{e}^-$	$E^\circ = -1.15 \text{ v}$
$\text{Au(c)} + 4 \text{Cl}^-(\text{aq}) = \text{AuCl}_4^-(\text{aq}) + 3 \text{e}^-$	$E^\circ = -1.00 \text{ v}$
$\text{AuCl}_2^-(\text{aq}) + 2 \text{Cl}^-(\text{aq}) = \text{AuCl}_4^-(\text{aq}) + 2 \text{e}^-$	$E^\circ = -0.93 \text{ v}$
$\text{Au(c)} + 2 \text{Br}^-(\text{aq}) = \text{AuBr}_2^-(\text{aq}) + \text{e}^-$	$E^\circ = -0.96 \text{ v}$
$\text{Au(c)} + 4 \text{Br}^-(\text{aq}) = \text{AuBr}_4^-(\text{aq}) + 3 \text{e}^-$	$E^\circ = -0.86 \text{ v}$
$\text{AuBr}_2^-(\text{aq}) + 2 \text{Br}^-(\text{aq}) = \text{AuBr}_4^-(\text{aq}) + 2 \text{e}^-$	$E^\circ = -0.80 \text{ v}$
$\text{Au(c)} + \text{I}^-(\text{aq}) = \text{AuI(c)} + \text{e}^-$	$E^\circ = -0.50 \text{ v}$
$\text{Au(c)} = \text{Au}^+(\text{aq}) + \text{e}^-$	$E^\circ \approx -1.7 \text{ v}$
$\text{Au(c)} + 3 \text{H}_2\text{O(l)} = \text{Au(OH)}_3(\text{c}) + 3 \text{H}^+(\text{aq}) + 3 \text{e}^-$	$E^\circ \approx -1.45 \text{ v}$
$2 \text{Au(c)} + 3 \text{H}_2\text{O(l)} = \text{Au}_2\text{O}_3(\text{c}) + 6 \text{H}^+(\text{aq}) + 6 \text{e}^-$	$E^\circ = -1.36 \text{ v}$
$\text{Au(c)} = \text{Au}^{+3}(\text{aq}) + 3 \text{e}^-$	$E^\circ \approx -1.50 \text{ v}$
$\text{Au}^+(\text{aq}) = \text{Au}^{+3}(\text{aq}) + 2 \text{e}^-$	$E^\circ \approx -1.4 \text{ v}$
$\text{Au(c)} + 2 \text{SCN}^-(\text{aq}) = \text{Au(SCN)}_2^-(\text{aq}) + \text{e}^-$	$E(1 \text{ M HCl}) = -0.69 \text{ v}$
$\text{Au(c)} + 4 \text{SCN}^-(\text{aq}) = \text{Au(SCN)}_4^-(\text{aq}) + 3 \text{e}^-$	$E(1 \text{ M HCl}) = -0.66 \text{ v}$
$\text{Au(SCN)}_2^-(\text{aq}) + 2 \text{SCN}^-(\text{aq}) = \text{Au(SCN)}_4^-(\text{aq}) + 2 \text{e}^-$	$E(1 \text{ M HCl}) = -0.64 \text{ v}$
$\text{Au(c)} + 2 \text{CN}^-(\text{aq}) = \text{Au(CN)}_2^-(\text{aq}) + \text{e}^-$	$E^\circ = 0.61 \text{ v}$



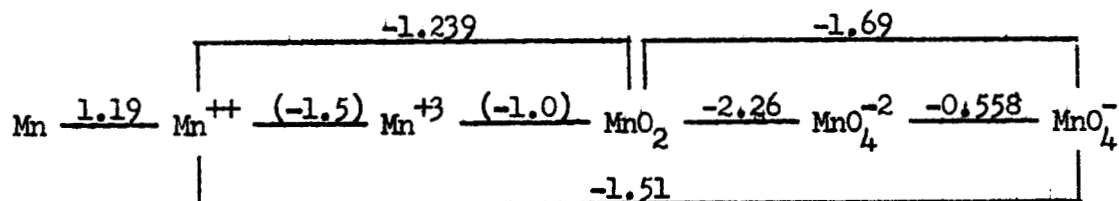
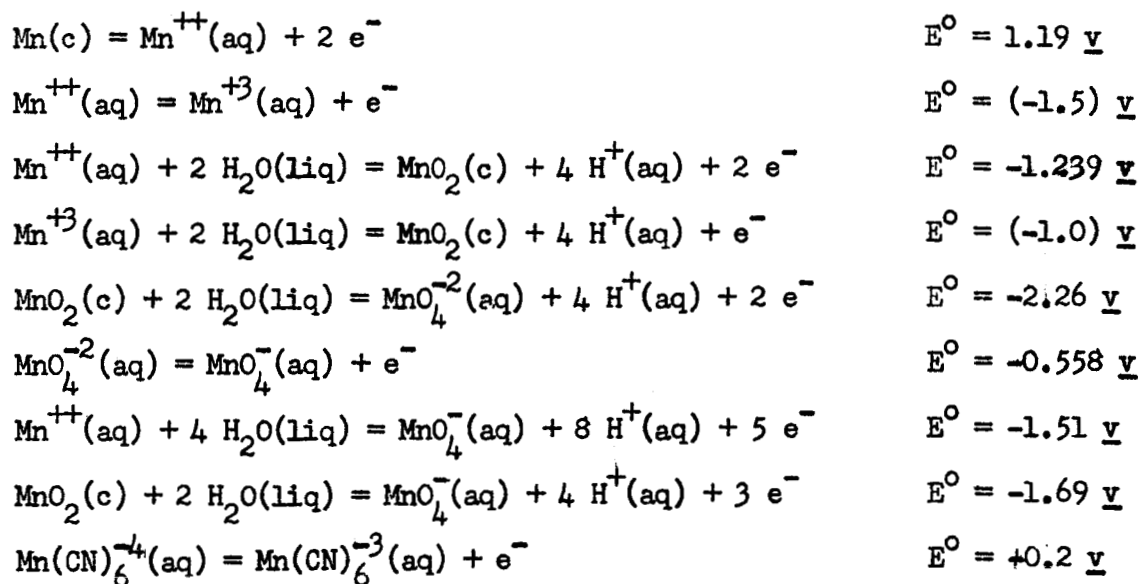
Iridium

Acidic solution:



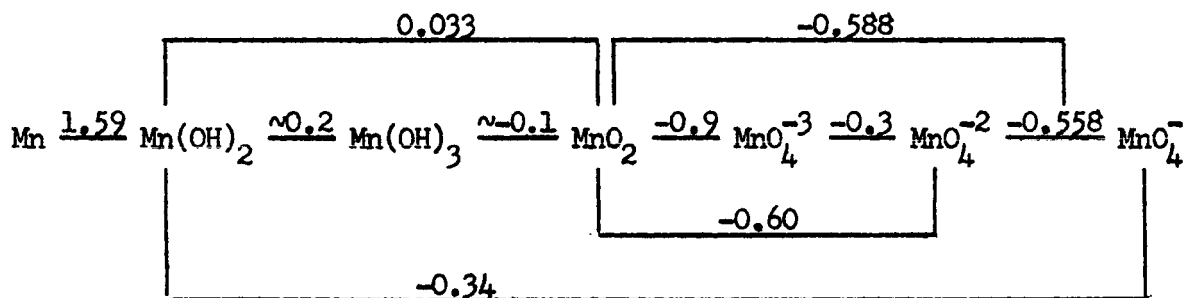
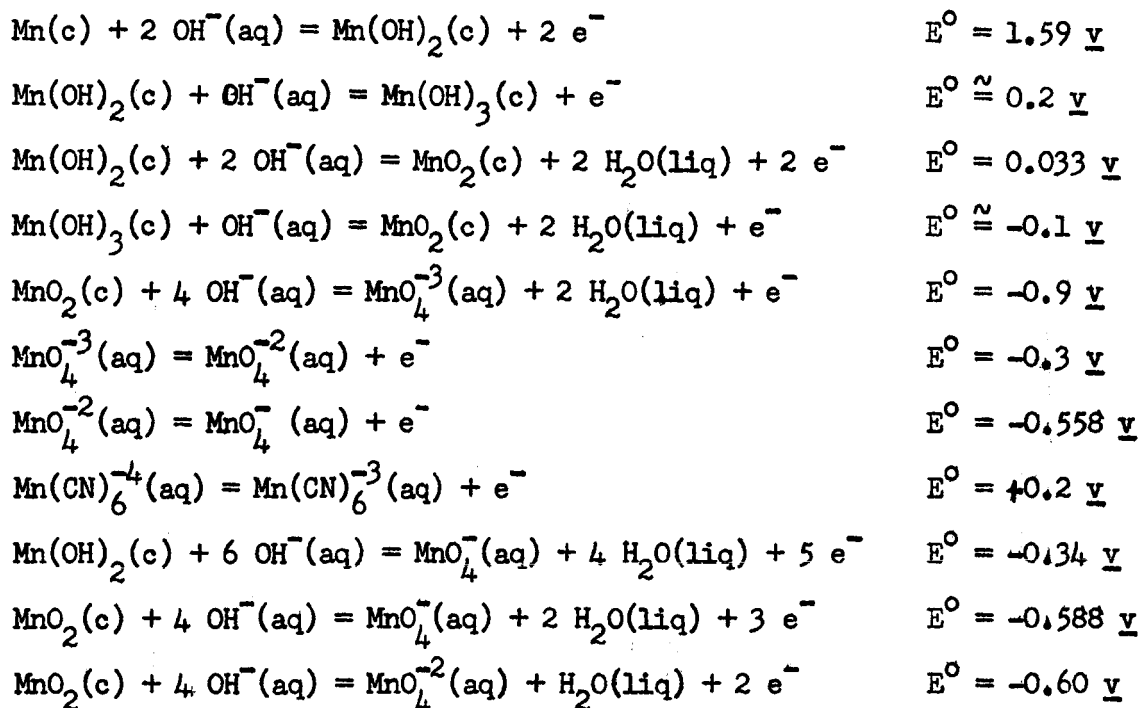
Manganese

Acidic solution:



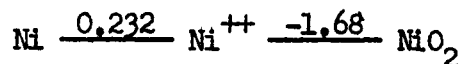
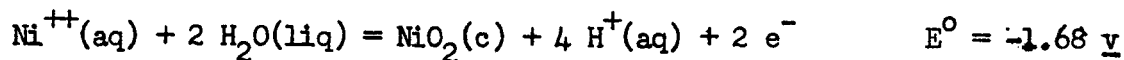
Manganese - continued

Basic solution:

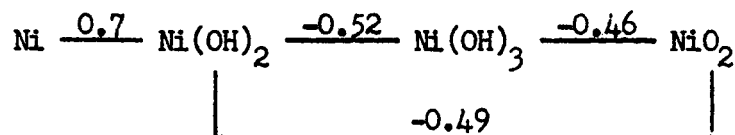
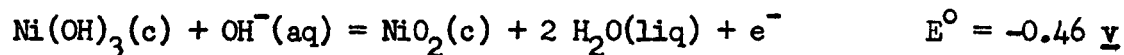
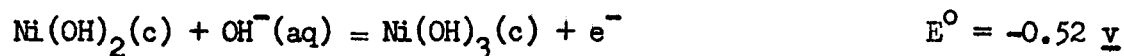
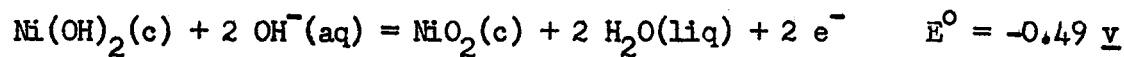
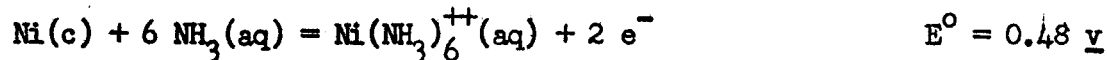
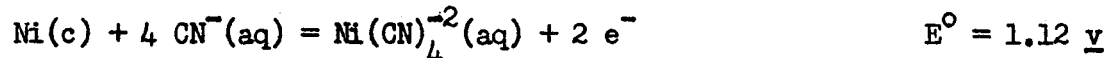
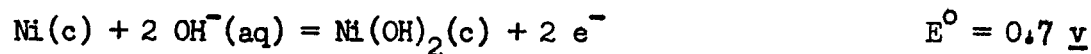


Nickel

Acidic solution:

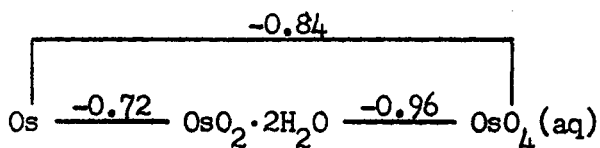
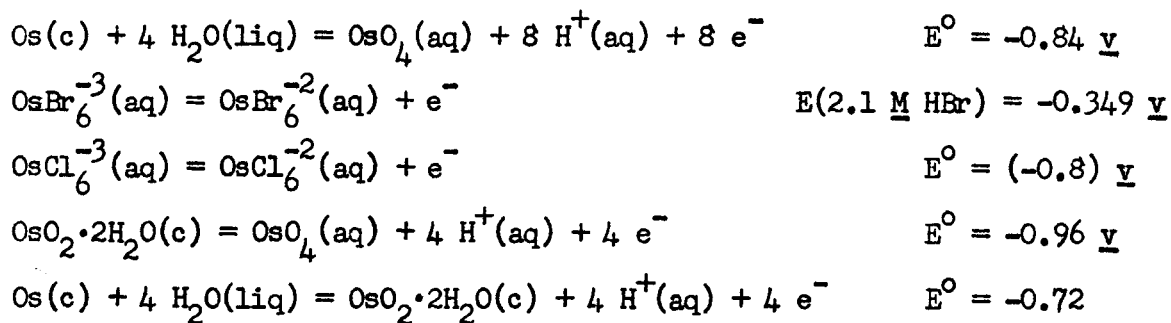


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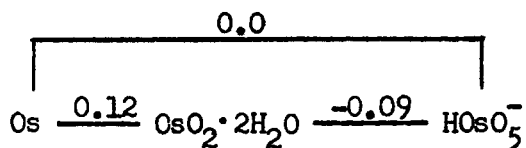
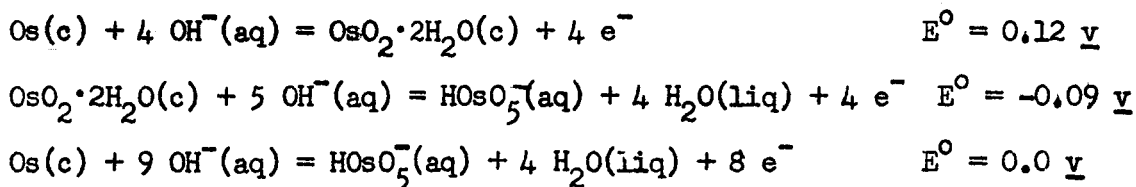


Osmium

Acidic solution:

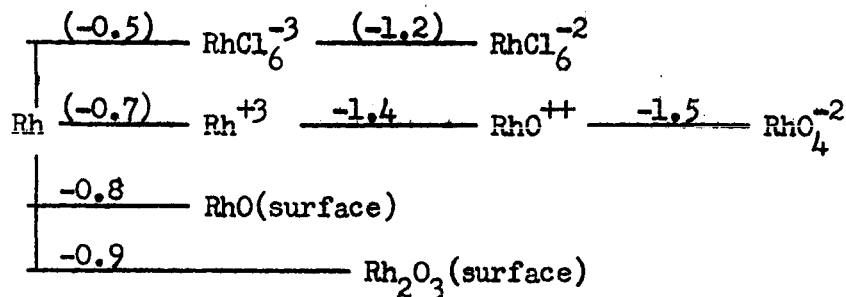
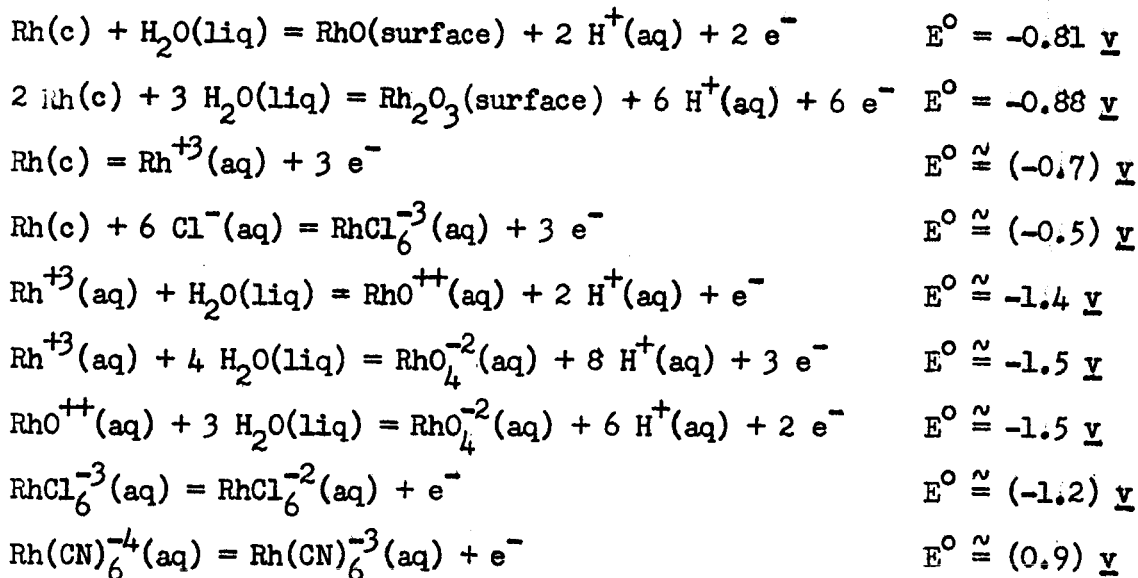


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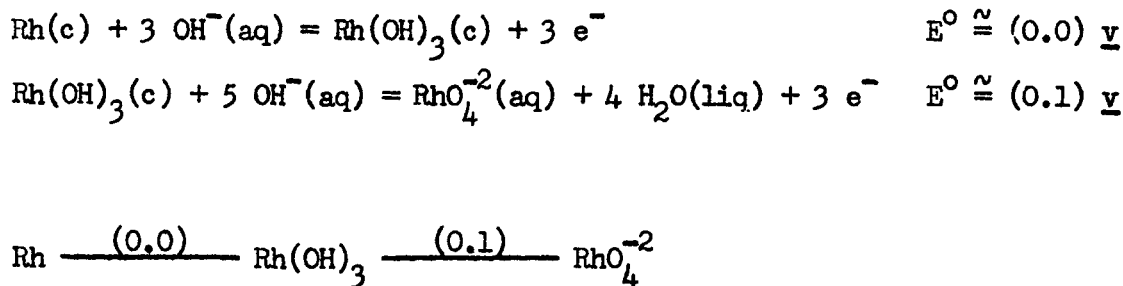


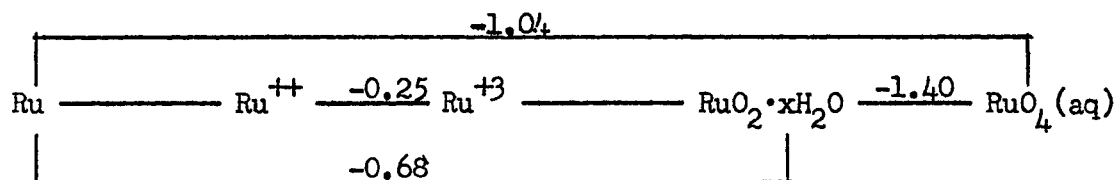
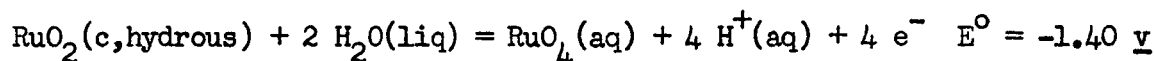
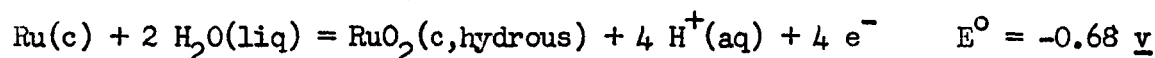
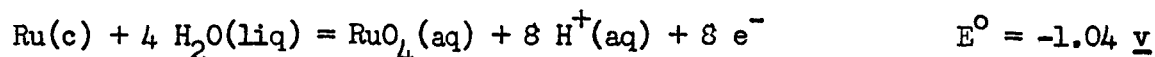
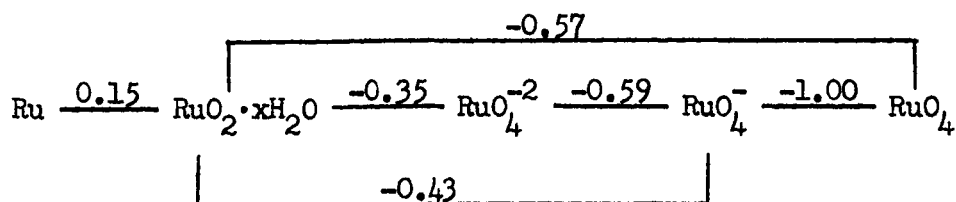
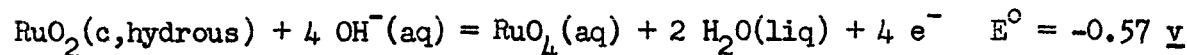
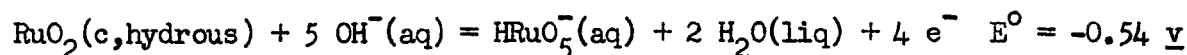
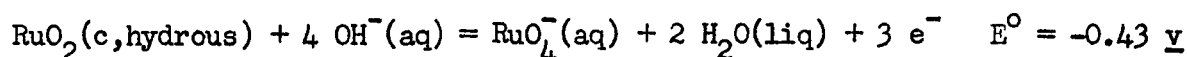
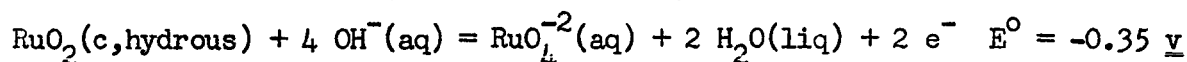
Rhodium

Acidic solution:



Basic solution:



$$\text{Ru}^{++}(\text{aq}) = \text{Ru}^{+3}(\text{aq}) + \text{e}^- \quad E^{\circ} = -0.249 \text{ v}$$

$$\text{Ru(c)} + 4 \text{ OH}^-(\text{aq}) = \text{RuO}_2(\text{c,hydrous}) + 2 \text{ H}_2\text{O}(\text{liq}) + 4 \text{ e}^- \quad E^\circ = 0.15 \text{ V}$$


Silver

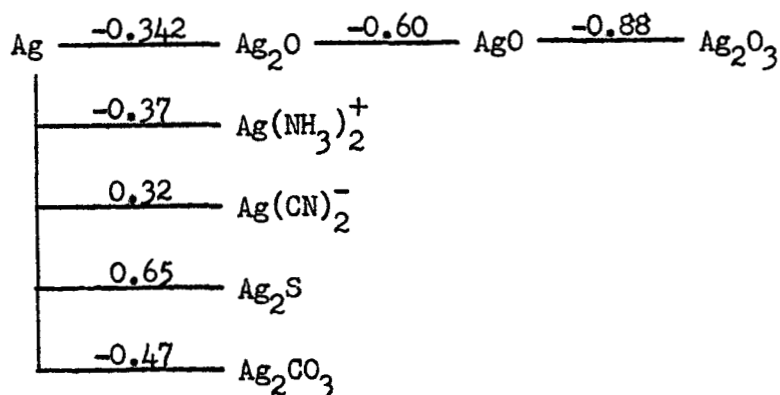
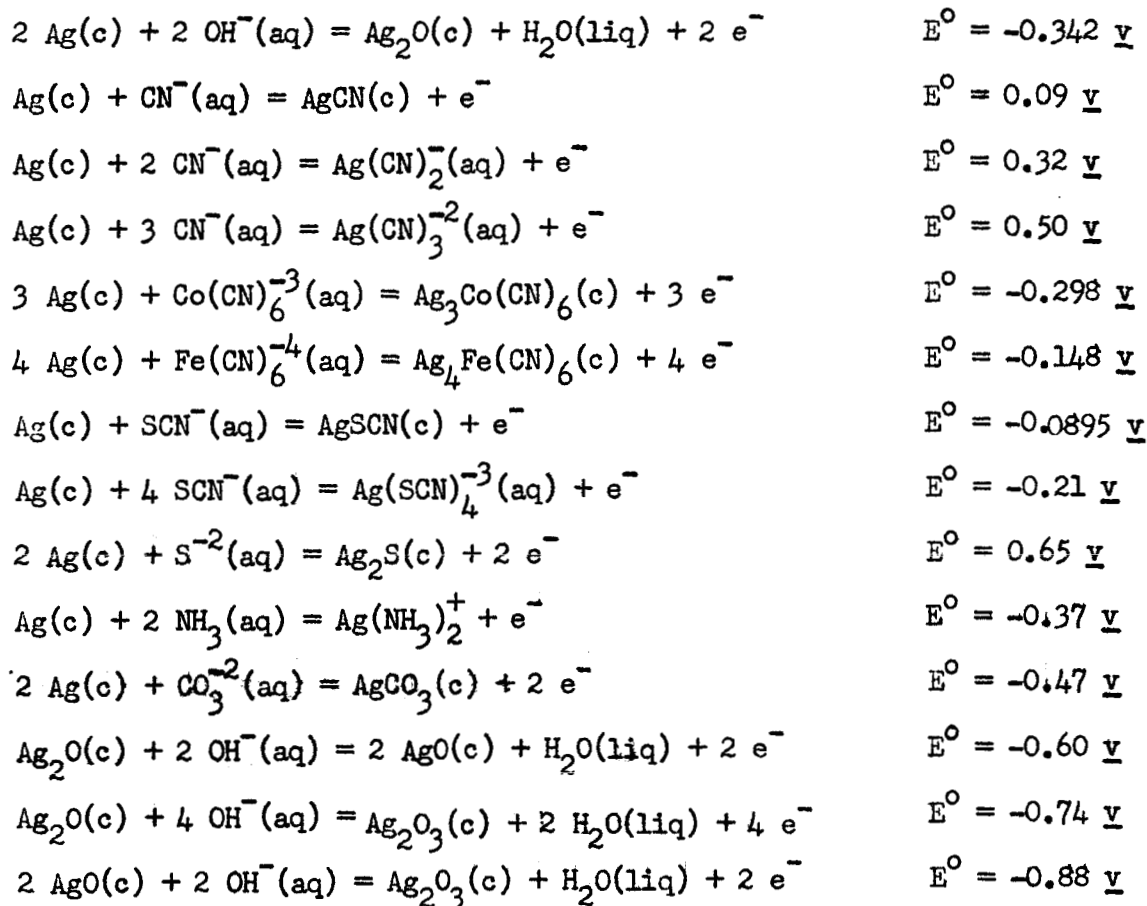
Acidic solution:

$\text{Ag(c)} = \text{Ag}^+(\text{aq}) + \text{e}^-$	$E^0 = -0.79931 \text{ v}$
$\text{Ag(c)} + \text{Cl}^-(\text{aq}) = \text{AgCl(c)} + \text{e}^-$	$E^0 = -0.22238 \text{ v}$
$\text{Ag(c)} + \text{Br}^-(\text{aq}) = \text{AgBr(c)} + \text{e}^-$	$E^0 = -0.0711 \text{ v}$
$\text{Ag(c)} + \text{I}^-(\text{aq}) = \text{AgI(c)} + \text{e}^-$	$E^0 = 0.152 \text{ v}$
$\text{Ag(c)} + \text{IO}_3^-(\text{aq}) = \text{AgIO}_3(\text{c}) + \text{e}^-$	$E^0 = -0.35 \text{ v}$
$2 \text{Ag(c)} + \text{H}_2\text{S(aq)} = \text{Ag}_2\text{S(c)} + 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$	$E^0 = 0.06 \text{ v}$
$\text{Ag}^+(\text{aq}) = \text{Ag}^{++}(\text{aq}) + \text{e}^-$	$E^0 \approx -1.98 \text{ v}$
$2 \text{Ag}^+(\text{aq}) + 3 \text{H}_2\text{O(liq)} = \text{Ag}_2\text{O}_3(\text{c}) + 6 \text{H}^+(\text{aq}) + 4 \text{e}^-$	$E^0 = -1.76 \text{ v}$
$2 \text{AgO(c)} + \text{H}_2\text{O(liq)} = \text{Ag}_2\text{O}_3(\text{c}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$	$E^0 = -1.71 \text{ v}$
$\text{Ag}^{++}(\text{aq}) + \text{H}_2\text{O(liq)} = \text{AgO}^+(\text{aq}) + 2 \text{H}^+(\text{aq}) + \text{e}^-$	$E^0 \approx -2.1 \text{ v}$
$\text{Ag}^+(\text{aq}) + \text{H}_2\text{O(liq)} = \text{AgO}^+(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$	$E^0 \approx -2.0 \text{ v}$

Ag	<u>-0.799</u>	Ag ⁺	<u>-1.98</u>	Ag ⁺⁺	<u>-2.1</u>	AgO ⁺
	<u>-0.222</u>	AgCl				
	<u>-0.071</u>	AgBr				
	<u>0.152</u>	AgI				
	<u>0.06</u>	Ag ₂ S				

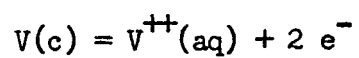
Silver continued

Basic solution:

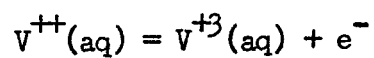


Vanadium

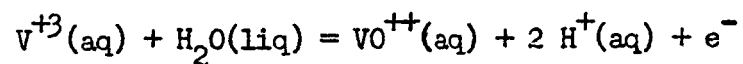
Acidic solution:



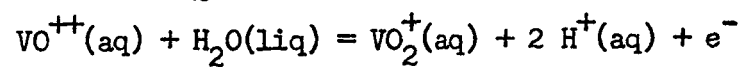
$$E^{\circ} = 1.12 \text{ v}$$



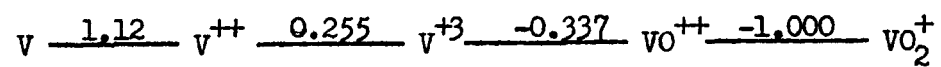
$$E^{\circ} = 0.255 \text{ v}$$



$$E^{\circ} = -0.337 \text{ v}$$



$$E^{\circ} = -1.000 \text{ v}$$



References

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