The Oxidation Potential of Cobaltous-Cobaltic Salts in Nitric Acid Solution

Thesis

by

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In Partial Fulfilment of the Requirements for
The Degree of Master of Science
in Chemistry

The California Institute of Technology
Pasadena
1936

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Introduction

The present determination of the cobaltous-cobaltic oxidation potential represents a continuation of a series of investigations, begun in this laboratory under the direction of Professor Noyes, on the oxidation potentials of strong oxidizing agents in nitric acid solution.[1,2,3] Previous work on this potential has been done by Oberer,[4] by Jahn,[5] and by Lamb and Larson.[6] All these investigators studied the same type of cell:

$$\mathrm{Pt} + \mathrm{H_2}(1\ \mathrm{atm.}),\ \mathrm{H_2SO_4}(c),\ \left\{\mathrm{H_2SO_4}(c) + \begin{matrix}\mathrm{CoSO_4}(c_1)\\ \mathrm{Co_2(SO_4)_3}(c_{\underline{2}})\end{matrix}\right\},\ \mathrm{Pt}$$

Jahn states that Oberer found that mixtures of cobaltous and cobaltic sulfates in dilute sulfuric acid give a potential "far above 1.7 volts" against the hydrogen electrode. In the cell studied by Jahn himself, the acid concentration (c) was 3 n and the total cobalt concentration $(c_1 + \underline{c}_2)$ 0.1 f. The potentials thus obtained were not corrected so as to refer the values to the standard molal hydrogen electrode. However, Lamb and Larson have estimated the activity of the hydrogen ion in 3 n sulfuric acid to be 1.2, and, applying this to Jahn's measurements, they have computed a value for the single cobaltous-cobaltic potential from his data.

In their own work Lamb and Larson used 4 n acid; they do not state the total cobalt concentration employed. In order to obtain the single cobaltous-cobaltic potential from measurements of this cell, it is necessary to eliminate the potential of the hydrogen electrode in 4 n sulfuric acid. This was done by measuring the electromotive force of a normal calomel cell against this hydrogen electrode, a saturated solution of ammonium nitrate being employed as a bridge between the two half-cells. However, no corrections were made for the liquid-junction potentials of this cell.

In order to avoid excessive decomposition of the cobaltic salt, all measurements were made at 0°. However, Lamb and Larson also made measurements at 16° and, by extrapolation, obtained a value for the potential at 25°.

The work of Noyes and Garner[2,3] indicates, at least in the case of ceric and thallic ions, that the tendency to form anion complexes is reduced to a minimum in nitrate solution; and accordingly, the potential obtained in such solutions represents more nearly the molal oxidation potential. In view of these facts and also of the fact that in the present series of investigations[1,2,3] nitric acid solutions have been used, it seemed desirable to study the cobaltous-cobaltic potential in the same acid. Moreover, the present study is made under more varied conditions than those of previous workers.

Therefore, there are described in this paper the measurements at 0° and 25° which have been made on cells of the type

$$Pt + H_2(1\ atm),\ HClO_4(c'),\ \left\{ HNO_3(c) + \begin{array}{l} Co^{II}(c_1) \\ Co^{III}(c_2) \end{array} \right\},\ Pt(or\ Au).$$

Since the cobaltic salt decomposes at a measurable rate at 0°, it has been possible to obtain some information on the kinetics of its decomposition. These results will be discussed briefly.

Apparatus and Materials

Preparation and Analysis of the Solutions. -

A stock solution approximately 0.5 f in cobaltous nitrate was prepared by dissolving Merck's Reagent $Co(NO_3)_2 \cdot 6\ H_2O$ (nickel free) in the proper quantity of distilled water. This solution was standardized gravimetrically (as $CoSO_4$). It was found to be 0.5239 f.

A stock solution of nitric acid was prepared by diluting c.p. nitric acid (sp. gr. 1.42). The resulting solution was standardized against a sodium hydroxide solution and was found to be 4.99 f.

Stock solutions containing cobaltous nitrate and nitric acid in different proportions were prepared by weighing out those quantities of these latter two solutions and of distilled water calculated to give the concentrations desired.

The cobalt in these stock solutions was partially converted into the trivalent form by electrolysis. The electrolytic cell used for this purpose was equipped with a platinum stirrer, which served also as the anode. The cathode, a small strip of platinum, was enclosed in a vessel resembling a small Gooch funnel inverted. A sintered glass plate prevented diffusion between the anode and cathode compartments. A current of about $\frac{3}{4}$ ampere at 6-8 volts was passed for a period 10-20% longer than that theoretically required to convert the cobalt entirely into the oxidized form. Since the electrolysis resulted in the transfer of some of the cobalt into the cathode compartment, it was necessary to blow the cathode solution back into the anode compartment after the current was turned off. Of course, since hydrogen ions were reduced at the cathode during the electrolysis, the acidity of the solution was no longer that which it was made up to be. Accordingly, if the resulting solution were desired to be, say, 0,1000 f in total cobalt and 3.0 f in nitric acid, the solution was made up initially 0.1000 f in cobalt and 3.1 f in acid.

The solutions of perchloric acid for the hydrogen half-cells were prepared by diluting the c.p. 60% acid, and they were standardized against a sodium hydroxide solution.

Calomel was prepared electrolytically by the method employed by Ellis.[7]

Tank hydrogen was purified by passing it first through a concentrated potassium hydroxide solution, then over solid potassium hydroxide, and finally over an electrically heated platinum wire.

<u>The Hydrogen Half-Cell</u>. - The hydrogen half-cell used was similar to that described by Noyes and Garner.[2] Before entering the cell the hydrogen gas was passed through a glass coil and then it was bubbled through perchloric acid of the same concentration as that in the half-cell. The apparatus was immersed in thermostats at 0.15±0.15° or 25.00±0.05°.

<u>Method of Potential Measurements</u>. - A Student's Type Leeds and Northrup potentiometer was used together with a high-sensitivity galvanometer.

After the completion of the electrolysis of a cobalt solution, the hydrogen half-cell was immersed in the solution. Previously the hydrogen electrode had been checked against a 1 n HCl calomel cell at the same temperature. Potential measurements were made over a period varying from 25 to 120 hours, depending upon the rate of decomposition of the trivalent cobalt, this being the greater the more dilute the acid. At frequent intervals samples were pipetted into previously weighed flasks containing an excess of ferrous sulfate. The flasks were again weighed and the excess ferrous sulfate titrated with permanganate. Since the pink color of the divalent cobalt interfered with the permanganate end-point, this was determined potentiometrically, using a vacuum tube voltmeter. The concentration of trivalent cobalt thereby determined was subtracted from the known total cobalt concentration in order to obtain that of the divalent form. In the case of the runs made at 0°, the pipettes used in withdrawing the cobalt solution had been chilled previously, as were the flasks containing the ferrous sulfate. Potential measurements were made immediately preceding the removal of the sample and again immediately afterwards. For the 0° experiments these checked to 0.1 millivolt. However, at 25°, where these frequently differed by as much as 1.5 millivolt, a mean was taken as corresponding to the potential at the time of withdrawal of the sample.

After the completion of the run, the hydrogen half-cell was removed from the remaining cobalt solution and again checked against the calomel cell.

The Observed and Calculated Electromotive Forces

Each of the following tables presents the data for one run. There are recorded the observed potential measurements, the corrections to be applied to these observed potentials, and the formal electrode potentials resulting therefrom.

In each table the first four columns present the concentrations of the various substances in the cells

Table I

The Observed and Calculated Electromotive Forces at 0°

HNO_3 c	$HClO_4$ c'	$Co(NO_3)_2$ c_1	$Co(NO_3)_3$ c_2	Co^{II}/Co^{III}	E_{obs} (Pt)	E_C	E_L	E_H	E° (Pt)
3.0 (α,0.85)	1.000 (α',0.803)	0.0396	0.0604	0.65	1.739	-0.010	+0.021	-0.005	1.744
		0.0667	0.0333	2.00	1.724	+0.016	+0.021	-0.005	1.756
		0.0656	0.0344	1.91	1.724	+0.015	+0.021	-0.005	1.755
		0.0661	0.0339	1.93	1.724	+0.016	+0.021	-0.005	1.754
		0.0675	0.0325	2.08	1.722	+0.017	+0.021	-0.005	1.755
		0.0681	0.0319	2.14	1.720	+0.018	+0.021	-0.005	1.754
		0.0715	0.0285	2.51	1.719	+0.022	+0.021	-0.005	1.756
		0.0739	0.0261	2.83	1.717	+0.025	+0.021	-0.005	1.757
		0.0795	0.0205	3.89	1.709	+0.032	+0.021	-0.005	1.757
		0.0838	0.0162	5.18	1.703	+0.039	+0.021	-0.005	1.757
								Mean	1.755

Table II

The Observed and Calculated Electromotive Forces at 0°

HNO_3	$HClO_4$	$Co(NO_3)_2$	$Co(NO_3)_3$	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
c	c'	c_1	c_2								
1.0 (α,0.71)	1.000 (α',0.803)	0.0299	0.0201	1.49	1.781	1.800	+0.009	-0.002	-0.005	1.783	1.802
		0.0340	0.0160	2.12	1.771	1.790	+0.018	-0.002	-0.005	1.781	1.800
		0.0367	0.0133	2.76	1.767	1.785	+0.024	-0.002	-0.005	1.783	1.801
		0.0426	0.0074	5.74	1.745	1.762	+0.041	-0.002	-0.005	1.779	1.794
		0.0434	0.0066	6.58	1.743	1.761	+0.044	-0.002	-0.005	1.780	1.798
									Mean	1.781	1.799

Table III

1.0 (α,0.71)	1.000 (α',0.803)	0.0298	0.0202	1.48	1.781	1.798	+0.009	-0.002	-0.005	1.783	1.800
		0.0332	0.0168	1.97	1.779	1.796	+0.016	-0.002	-0.005	1.787	1.804
		0.0408	0.0092	4.43	1.758	1.776	+0.035	-0.002	-0.005	1.785	1.803
		0.0423	0.0077	5.53	1.750	1.768	+0.040	-0.002	-0.005	1.782	1.800
		0.0436	0.0064	6.85	1.743	1.751	+0.045	-0.002	-0.005	1.781	1.799
		0.0449	0.0051	8.84	1.734	1.754	+0.051	-0.002	-0.005	1.778	1.798
									Mean	1.783	1.801

Table IV

The Observed and Calculated Electromotive Forces at 0°

HNO_3 c	$HClO_4$ c'	$Co(NO_3)_2$ c_1	$Co(NO_3)_3$ c_2	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
1.0 (α,0.71)	1.000 (α',0.803)	0.0292	0.0208	1.41	1.780	1.797	+0.008	-0.002	-0.005	1.781	1.798
		0.0400	0.0100	3.99	1.756	1.773	+0.033	-0.002	-0.005	1.781	1.798
		0.0410	0.0090	4.54	1.754	1.772	+0.036	-0.002	-0.005	1.782	1.800
		0.0423	0.0077	5.53	1.749	1.768	+0.040	-0.002	-0.005	1.782	1.801
		0.0431	0.0069	6.23	1.743	1.762	+0.043	-0.002	-0.005	1.779	1.799
		0.0453	0.0047	9.75	1.731	1.750	+0.054	-0.002	-0.005	1.777	1.796
		0.0460	0.0040	11.4	1.730	1.750	+0.057	-0.002	-0.005	1.779	1.799
									Mean	1.780	1.799
								General	mean	1.781	1.800

Table V

The Observed and Calculated Electromotive Forces at 0°

HNO_3 *c*	$HClO_4$ *c'*	$Co(NO_3)_2$ c_1	$Co(NO_3)_3$ c_2	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
2.0 (α, 0.76)	1.000 (α', 0.803)	0.0273	0.0477	0.57	1.806	1.814	-0.010	+0.012	-0.005	1.802	1.810
		0.0349	0.0401	0.87	1.796	1.804	-0.003	+0.012	-0.005	1.800	1.808
		0.0499	0.0251	1.99	1.772	1.780	+0.016	+0.012	-0.005	1.795	1.803
		0.0517	0.0233	2.22	1.770	1.778	+0.019	+0.012	-0.005	1.796	1.804
		0.0547	0.0203	2.70	1.765	1.773	+0.023	+0.012	-0.005	1.795	1.803
		0.0578	0.0172	3.36	1.761	1.769	+0.029	+0.012	-0.005	1.796	1.805
		0.0626	0.0124	5.09	1.749	1.757	+0.038	+0.012	-0.005	1.794	1.802
									Mean	1.797	1.805

Table VI

The Observed and Calculated Electromotive Forces at 0°

HNO_3	$HClO_4$	$Co(NO_3)_2$	$Co(NO_3)_2$	Co^{II}/Co^{III}	E_{obs} (PT)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
c	c'	c_1	c_2								
2.0 (α,0.76)	1.000 (α',0.803)	0.0368	0.0382	0.97	1.790	1.798	-0.001	+0.012	-0.005	1.796	1.804
		0.0474	0.0276	1.71	1.779	1.788	+0.013	+0.012	-0.005	1.799	1.807
		0.0495	0.0255	1.94	1.777	1.785	+0.016	+0.012	-0.005	1.799	1.807
		0.0524	0.0226	2.33	1.775	1.782	+0.020	+0.012	-0.005	1.801	1.808
		0.0560	0.0190	2.95	1.767	1.775	+0.026	+0.012	-0.005	1.799	1.807
		0.0581	0.0169	3.45	1.761	1.770	+0.029	+0.012	-0.005	1.797	1.805
		0.0613	0.0137	4.47	1.756	1.765	+0.035	+0.012	-0.005	1.798	1.807
									Mean	1.798	1.807
								General	mean	1.798	1.806

Table VII

The Observed and Calculated Electromotive Forces at 0°

HNO_3	$HClO_4$	$Co(NO_3)_2$	$Co(NO_3)_3$	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
c	c'	c_1	c_2								
3.0 (α,0.85)	1.000 (α',0.803)	0.0231	0.0269	0.86	1.791	1.798	-0.004	+0.021	-0.005	1.803	1.810
		0.0237	0.0263	0.91	1.790	1.797	-0.002	+0.021	-0.005	1.803	1.810
		0.0245	0.0255	0.96	1.788	1.795	-0.001	+0.021	-0.005	1.802	1.809
		0.0272	0.0228	1.19	1.783	1.790	+0.004	+0.021	-0.005	1.803	1.810
		0.0284	0.0216	1.31	1.779	1.786	+0.006	+0.021	-0.005	1.801	1.808
		0.0295	0.0205	1.45	1.779	1.787	+0.009	+0.021	-0.005	1.803	1.811
		0.0305	0.0195	1.56	1.775	1.783	+0.011	+0.021	-0.005	1.801	1.809
		0.0327	0.0173	1.90	1.767	1.775	+0.015	+0.021	-0.005	1.798	1.806
		0.0338	00.0162	2.10	1.766	1.774	+0.017	+0.021	-0.005	1.799	1.807
		0.0347	0.0153	2.26	1.765	1.773	+0.019	+0.021	-0.005	1.799	1.807
		0.0376	0.0124	3.04	1.755	1.763	+0.026	+0.021	-0.005	1.797	1.805
		0.0388	0.0112	3.48	1.756	1.765	+0.029	+0.021	-0.005	1.801	1.810
		0.0412	0.0088	4.66	1.746	1.754	+0.036	+0.021	-0.005	1.798	1.806
									Mean	1.801	1.808

Table VIII

The Observed and Calculated Electromotive Forces at 0°

HNO_3 c	$HClO_4$ c'	$Co(NO_3)_2$ c_1	$Co(NO_3)_3$ c_2	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
3.0 (α, 0.85)	1.000 (α', 0.803)	0.0118	0.0382	0.31	1.811	1.818	-0.028	+0.021	-0.005	1.799	1.806
		0.0153	0.0347	0.42	1.806	1.813	-0.019	+0.021	-0.005	1.802	1.809
		0.0182	0.0318	0.52	1.801	1.808	-0.015	+0.021	-0.005	1.801	1.808
		0.0192	0.0308	0.62	1.798	1.805	-0.011	+0.021	-0.005	1.802	1.809
		0.0286	0.0214	1.33	1.779	1.787	+0.007	+0.021	-0.005	1.801	1.809
		0.0317	0.0183	1.87	1.772	1.780	+0.015	+0.021	-0.005	1.802	1.809
		0.0332	0.0168	1.98	1.768	1.776	+0.016	+0.021	-0.005	1.800	1.808
									Mean	1.801	1.808
								General	mean	1.801	1.808

Table IX

The Observed and Calculated Electromotive Forces at 0°

HNO_3 c	$HClO_4$ c'	$Co(NO_3)_2$ c_1	$Co(NO_3)_3$ c_2	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
3.0 (α,0.85)	1.000 (α',0.803)	0.0348	0.0652	0.53	1.803	1.810	-0.015	+0.021	-0.005	1.804	1.811
		0.0381	0.0619	0.62	1.800	1.807	-0.011	+0.021	-0.005	1.804	1.811
		0.0406	0.0594	0.68	1.797	1.804	-0.009	+0.021	-0.005	1.803	1.810
		0.0430	0.0570	0.75	1.796	1.803	-0.006	+0.021	-0.005	1.804	1.811
		0.0451	0.0549	0.82	1.794	1.802	-0.005	+0.021	-0.005	1.805	1.813
		0.0590	0.0410	1.44	1.780	1.788	+0.009	+0.021	-0.005	1.804	1.812
		0.0610	0.0390	1.57	1.777	1.785	+0.011	+0.021	-0.005	1.804	1.812
		0.0628	0.0372	1.69	1.776	1.783	+0.012	+0.021	-0.005	1.804	1.811
		0.0644	0.0356	1.81	1.775	1.783	+0.014	+0.021	-0.005	1.804	1.812
		0.0656	0.0344	1.91	1.774	1.782	+0.015	+0.021	-0.005	1.804	1.812
		0.0669	0.0331	2.02	1.773	1.780	+0.017	+0.021	-0.005	1.804	1.812
		0.0679	0.0321	2.12	1.772	1.780	+0.018	+0.021	-0.005	1.805	1.813
		0.0745	0.0255	2.92	1.762	1.770	+0.025	+0.021	-0.005	1.803	1.811
									Mean	1.804	1.812

Table X

The Observed and Calculated Electromotive Forces at 0°

HNO_3 c	$HClO_4$ c'	$Co(NO_3)_2$ c_1	$Co(NO_3)_3$ c_2	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
3.0 (α, 0.85)	1.000 (α', 0.803)	0.0340	0.0660	0.52	1.803	1.810	−0.016	+0.021	−0.005	1.802	1.809
		0.0367	0.0633	0.58	1.802	1.809	−0.013	+0.021	−0.005	1.805	1.812
		0.0408	0.0592	0.69	1.799	1.806	−0.009	+0.021	−0.005	1.805	1.812
		0.0452	0.0548	0.83	1.793	1.800	−0.005	+0.021	−0.005	1.803	1.811
		0.0674	0.0326	2.07	1.772	1.779	+0.017	+0.021	−0.005	1.804	1.811
		0.0681	0.0319	2.14	1.771	1.779	+0.018	+0.021	−0.005	1.804	1.812
		0.0744	0.0256	2.90	1.763	1.771	+0.025	+0.021	−0.005	1.804	1.812
		0.0761	0.0239	3.19	1.761	1.769	+0.027	+0.021	−0.005	1.803	1.811
		0.0767	0.0233	3.30	1.760	1.768	+0.028	+0.021	−0.005	1.803	1.811
		0.0775	0.0225	3.45	1.59	1.767	+0.029	+0.021	−0.005	1.803	1.811
		0.0792	0.0208	3.80	1.756	1.764	+0.032	+0.021	−0.005	1.803	1.811
		0.0794	0.0206	3.85	1.755	1.763	+0.032	+0.021	−0.005	1.802	1.811
		0.0840	0.0160	5.40	1.749	1.757	+0.040	+0.021	−0.005	1.804	1.812
									Mean	1.804	1.811
								General	mean	1.804	1.811

Table XI

The Observed and Calculated Electromotive Forces at 0°

HNO_3	$HClO_4$	$Co(NO_3)_2$	$Co(NO_3)_3$	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
c	c'	c_1	c_2								
4.0 (α,0.96)	2.000 (α',1.295)	0.0243	0.0757	0.31	1.806	1.810	-0.027	+0.007	+0.022	1.808	1.812
		0.0276	0.0724	0.38	1.804	1.808	-0.022	+0.007	+0.022	1.810	1.814
		0.0451	0.0549	0.82	1.788	1.792	-0.005	+0.007	+0.022	1.812	1.816
		0.0481	0.0519	0.93	1.786	1.790	-0.002	+0.007	+0.022	1.813	1.817
		0.0502	0.0498	1.01	1.783	1.787	0.000	+0.007	+0.022	1.811	1.815
		0.0520	0.0480	1.09	1.781	1.785	+0.002	+0.007	+0.022	1.811	1.815
		0.0592	0.0408	1.45	1.774	1.778	+0.009	+0.007	+0.022	1.812	1.816
		0.0617	0.0383	1.61	1.772	1.776	+0.011	+0.007	+0.022	1.812	1.816
		0.0654	0.0346	1.89	1.767	1.772	+0.015	+0.007	+0.022	1.811	1.816
		0.0715	0.0285	2.51	1.760	1.765	+0.022	+0.007	+0.022	1.811	1.816
		0.0740	0.0260	2.84	1.757	1.762	+0.025	+0.007	+0.022	1.811	1.816
		0.0777	0.0223	3.50	1.752	1.757	+0.030	+0.007	+0.022	1.811	1.816
									Mean	1.811	1.816

Table XII

The Observed and Calculated Electromotive Forces at 25°

HNO_3 c	$HClO_4$ c'	$Co(NO_3)_2$ c_1	$Co(NO_3)_3$ c_2	Co^{II}/Co^{III}	E_{obs} (Pt)	E_{obs} (Au)	E_C	E_L	E_H	E° (Pt)	E° (Au)
3.0 (α,0.85)	2.000 (α',1.295)	0.0782	0.0218	3.60	1.759	1.790	+0.030	0.000	+0.024	1.813	1.844
		0.0850	0.0150	5.67	1.746	1.780	+0.041	0.000	+0.024	1.811	1.844
		0.0884	0.0116	7.64	1.736	1.771	+0.048	0.000	+0.024	1.808	1.843
		0.0912	0.0088	10.4	1.727	1.764	+0.055	0.000	+0.024	1.806	1.843
		0.0935	0.0065	14.5	1.714	1.754	+0.063	0.000	+0.024	1.801	1.841
		0.0958	0.0042	22.8	1.696	1.741	+0.073	0.000	+0.024	1.794	1.838
									Mean	1.805	1.842

Table XIII

4.0 (α,0.96)	2.000 (α',1.295)	0.0797	0.0203	3.94	1.766	1.788	+0.032	+0.007	+0.024	1.830	1.852
		0.0834	0.0166	5.04	1.760	1.782	+0.038	+0.007	+0.024	1.829	1.852
		0.0866	0.0134	6.45	1.753	1.776	+0.044	+0.007	+0.024	1.828	1.852
		0.0890	0.0110	8.10	1.746	1.770	+0.049	+0.007	+0.024	1.827	1.851
		0.0909	0.0091	9.95	1.739	1.764	+0.054	+0.007	+0.024	1.824	1.850
		0.0923	0.0077	12.0	1.733	1.759	+0.059	+0.007	+0.024	1.823	1.848
		0.0939	0.0061	15.4	1.726	1.753	+0.064	+0.007	+0.024	1.822	1.848
									Mean	1.826	1.850

expressed in formula-weights per 1000 grams of water (that is, their weight-formalities). In the fifth column are given the ratios of divalent to trivalent cobalt. The sixth and seventh columns give the observed potentials against platinum and gold, respectively. The activity coefficients (α and α') of the two acids are given below their concentrations. The values at 25° are those of Abel, Redlich, and v. Lengyel[8] for nitric acid and those of Pearce and Nelson[9] for perchloric acid. Inasmuch as there are no data available at 0°, these same values are used at this latter temperature.

The columns labelled E_C, E_L, and E_H contain the corrections which are added to the observed potential E_{obs} to give the formal electrode potential E^0.

The quantity $E_C = (RT/2F) \ln(c_1/c_2)$ is applied so as to provide for equiformal concentrations of cobaltous and cobaltic cobalt. Since their activities are not known, the total concentrations c_1 and c_2 are used.

The quantity $E_L = (2T_H-1)(RT/F) \ln(\alpha c/\alpha' c')$ is applied in order to eliminate the liquid potential to the extent that this arises from the different ion activities αc and $\alpha' c'$ of the two acids. The ion mobilities are here considered to be equal. The mean transference number T_H of the cation of the two acids has been estimated to be 0.85 at 25° and 0.87 at 0°.

The quantity $E_H = (RT/F)\ \ln(\alpha'c')/\sqrt{p_{H_2}}$ is added in order to refer the value to the standard molal hydrogen electrode H_2 (1 atm.), H^+ (activity 1 m).

The formal electrode potential E^0 thus obtained is considered to be equal to that of the cell

$$Pt+H_2(1\ \text{atm}),\ H^+(1\ m)\Big\|\left\{HNO_3(1\ \text{to}\ 4\ f)+\begin{matrix}Co^{II}(1\ f)\\ Co^{III}(1\ f)\end{matrix}\right\},\ Pt(\text{or}\ Au).$$

Discussion of the Potential Measurements

The EMF in Relation to the Type of Electrode. - Jahn[5] experienced considerable difficulty in obtaining constant and reproducible results. Different platinum electrodes of the same area and thickness which had been cleaned in the same manner, were found to give potentials differing by several centivolts. Moreover, the time required to reach equilibrium with the solution varied from a few hours to several days. However, he found that if an electrode were removed from a cobalt solution, the moisture adhering to it allowed to evaporate, and the residue remaining on the electrode ignited to form cobalt oxide (probably Co_3O_4), reproducible and fairly constant results could be obtained with it. Nickel oxide behaved similarly.

Lamb and Larson[6] likewise used a platinum foil coated with cobalt oxide. However, they found that a gold electrode gave a higher potential.

In the present investigation the author encountered the same trouble as did Jahn. The difficulty lay largely in the fact that electrodes were very slow in coming to equilibrium. However, it was found that the platinum stirrer, which functioned as the anode in the electrolytic oxidation of the cobaltous solution, gave a reproducible and constant E° if it were lightly platinized. Table I presents the data from a typical run using the platinum stirrer as the electrode.

Knowing that silver establishes its potential quite readily, Dr. C. D. Coryell suggested its use as a potential mediator. Accordingly, a drop (1/28 ml) of 1n $AgNO_3$ was added to about 225 ml of the oxidized cobalt solution. The observed potential immediately increased. A second drop caused a further increase. After the addition of about ten drops, the potential no longer rose. The same effect was observed for a gold electrode, except that only about half as much $AgNO_3$ was required to attain the maximum potential. Figures 1 and 2 show graphically these effects. It will be noted that this maximum potential for gold is somewhat higher than that for platinum. In 1 n acid this difference at 0° is about 20 millivolts, while in 4 n acid it amounts to about 5 millivolts. Strangely enough, the difference at 25° in the latter acid is about 25 millivolts. As the trivalent cobalt decomposed, this difference increased slightly.

It is interesting to note that if not enough $AgNO_3$ were added to reach the maximum potential for plati-

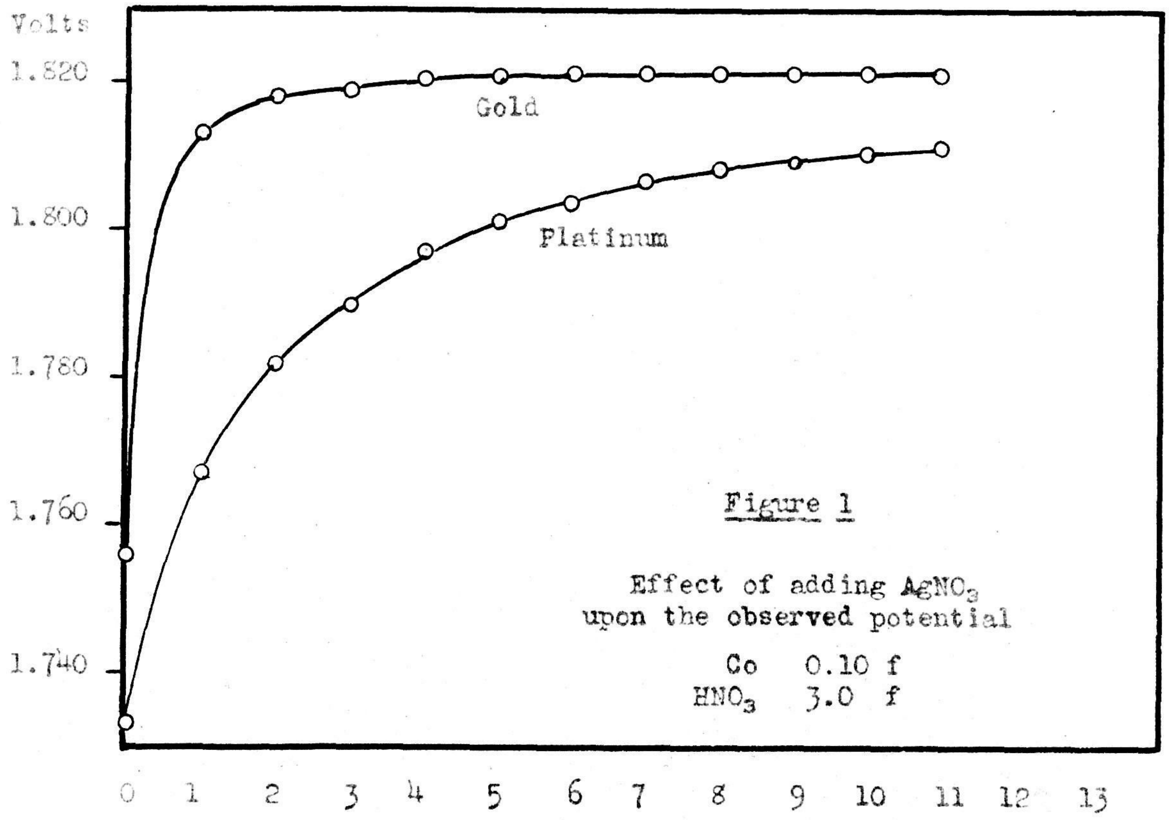

Figure 1

Effect of adding $AgNO_3$
upon the observed potential

Co 0.10 f
HNO_3 3.0 f

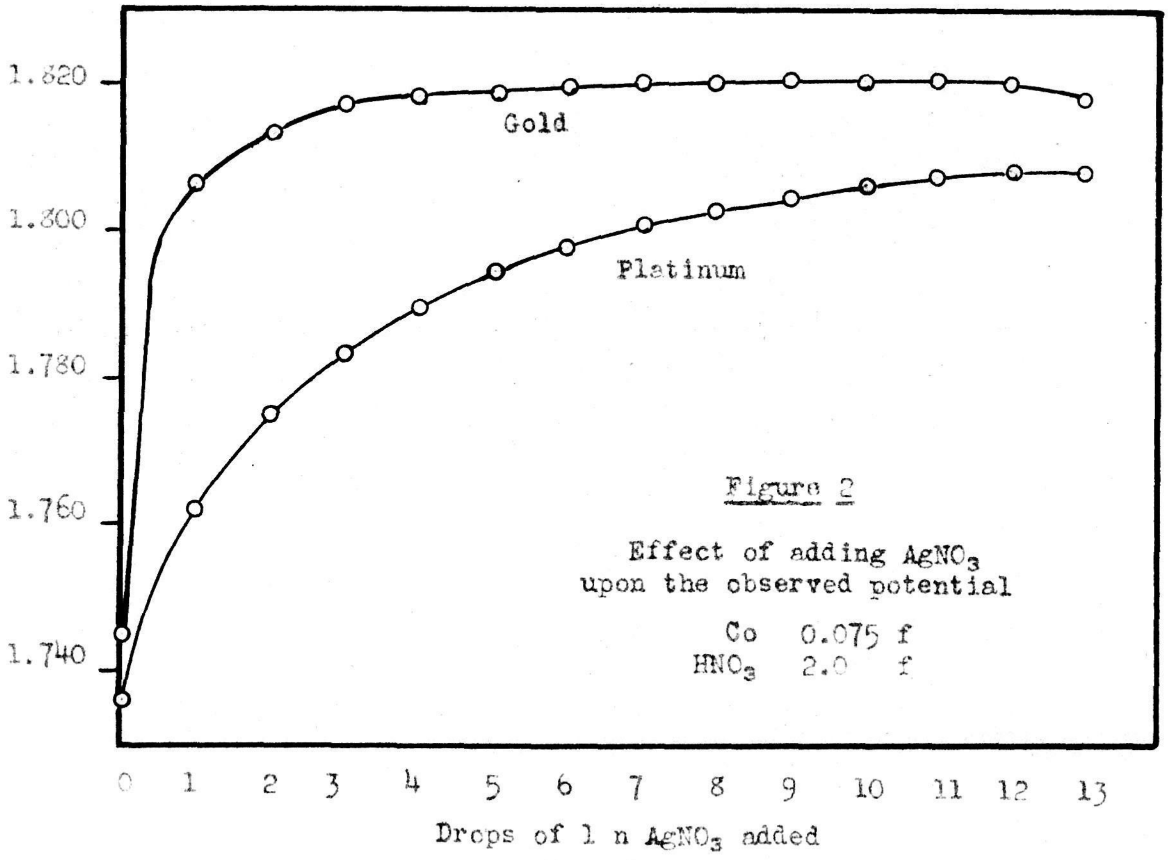

Figure 2

Effect of adding $AgNO_3$
upon the observed potential

Co 0.075 f
HNO_3 2.0 f

num, but yet sufficient to attain that for gold, the observed potential for platinum increased over a certain period as the trivalent cobalt decomposed, whereas the observed potential for gold decreased in accordance with the Nernst equation.

Before the addition of $AgNO_3$ the potential observed for the gold electrode was usually, but not always, higher than that for platinum. In the case of 1 n nitric acid, the gold electrode gave a potential slightly lower than that for platinum. In 2 n acid the former was about 10 millivolts higher; in 3 n acid, about 25 millivolts; and in 4 n acid, about 40 millivolts.

In order to note the effect of the added $AgNO_3$ upon E^o, Table I should be compared with Tables IX and X.

The amount of $AgNO_3$ solution which was added varied from 8 to 13 drops (1/28 ml) to a volume of about 225-250 ml of cobalt solution. The stronger the acid and the more rapidly the drops were added, the greater was the total number of drops required to reach the maximum potential.

Effect of Stirring upon the Observed Potential. - Before the addition of the silver nitrate, the observed potential with platinum was from one to two millivolts lower when the solution was stirred. After it was added, the potential with stirring was from three to five millivolts higher than without. In the case of the gold electrode, stirring increased the potential half a millivolt, both before and after the addition of the silver nitrate.

Effect of Adding Nickel Nitrate. - It was thought that nickel nitrate might have an effect similar to that of silver nitrate. Accordingly, one drop of 1 n nickelous nitrate was added to a cobalt solution. The potential immediately dropped about 20 millivolts in the case of platinum, while with gold the decrease was only about 2 millivolts. After the solution was allowed to stand about 20 minutes, the potentials came back to their previous values.

In view of the facts that the gold electrode gives a slightly more constant E^0 than platinum, that stirring is practically without effect upon the potential, that it comes to equilibrium more rapidly (as indicated by the fact that less silver nitrate is required to attain the maximum potential), and finally, that it gives a higher potential than platinum, the values recorded for gold are believed to represent more nearly the cobaltous-cobaltic potential. Moreover, the smaller difference in E^0 in going from 1 n to 4 n acid (30 millivolts for platinum and 16 millivolts for gold) favors the use of the values obtained with the gold electrode.

The existence of this difference may be accounted for in any of several ways. In the lower acid strengths there may occur a hydrolysis of the cobaltic salt by a reaction like $Co^{+++} + H_2O = CoO^+ + 2H^+$. Or with increasing ionic strength the activity coefficient of the cobaltic ion may increase more rapidly than does that of the cobaltous ion. Or the cobaltous ion may form nitrate complexes more rapidly than does the cobaltic ion with increasing nitrate concentration. However, since the complexes of the cobaltous ion are so unstable,[10] this last explanation does not seem to be a very probable one.

It might be thought that a large part of this difference may be due to the inadequacy of the liquid junction correction E_L. Accordingly, in one run in which 3 n nitric acid was employed, potential measurements were made first with a 1 n $HClO_4$ hydrogen electrode and then with a 2 n $HClO_4$ electrode. The average of the E^o's calculated from the potentials observed with the latter electrode was only half a millivolt higher than those obtained using the 1 n electrode. Noyes and Kossiakoff[1] have tested the reliability of the correction when the nitric and perchloric acids are both 1 molal (activity).

In the following table are summarized the results of the present investigation, the values recorded being those for the gold electrode.

Temperature	0°	0°	0°	0°	0°	25°	25°
HNO_3	1.0	2.0	3.0	3.0	4.0	3.0	4.0
Total Co	0.05	0.075	0.05	0.1	0.1	0.1	0.1
Co^{II}/Co^{III}	0.36-11.4	0.57-5.1	0.86-4.7	0.52-5.4	0.31-3.5	3.6-22.8	3.9-15.4
E^o	1.800	1.806	1.808	1.811	1.816	1.842	1.850
Mean deviation	±0.002	±0.002	±0.001	±0.001	±0.001	±0.002	±0.002

The values at 0° obtained by Lamb and Larson[6] from Jahn's[5] data in 3 n sulfuric acid and by themselves in 4 n sulfuric acid are 1.779 and 1.775 volts, respectively. At 25° Lamb and Larson obtained 1.817 volts. It is possible that the difference between these results and those of the present investigation may be accounted for on the basis of complex formation between the cobaltic ion and the sulfate or hydrosulfate ion. However, due to uncertainties in eliminating the potential of the hydrogen electrode in 3 n and 4 n sulfuric acid, too much significance cannot be attached to this relatively small difference of 25 or 30 millvolts.

The kinetic activity of the argentic ion appears to be considerably greater than that of the cobaltic ion. When solutions containing approximately equivalent quantities of cobaltic and manganous salts are mixed, there immediately appears a brown color in the solution, indicating the formation of manganese dioxide. After half an hour, the color of permanganate is apparent. However, if a drop of silver nitrate solution is added after the two solutions are mixed, the color of permanganate immediately appears. In the case of chromic and cobaltic salts, the color of the solution after 24 hours appears to have changed little, if any, from the greenish blue of the cobaltic ion. If a drop of silver nitrate is then added, the color soon becomes a yellowish green and after about 30 minutes the color is almost the pure yellow of dichromate.

Discussion of the Kinetics of the Decomposition of Cobaltic Nitrate by Water

Figures 3, 4, 5 and 6 present graphically the data of Tables VII, IX, X and XI. The abscissae represent the time in hours at which samples were withdrawn, the time of removal of the first one being taken as zero. The ordinates represent the reciprocals of the cobaltic concentrations and the logarithms of these quantities. It was found that, in general, the rate of decomposition is second order with respect to the cobaltic concentration during the first part of the run, and first order during the latter, this being the case whether or not silver is present.

Figures 4, 5 and 6 are typical of the results obtained. However, there are exceptions. In the case of Figure 3 the decomposition is first order throughout. In contrast the data of Table VI give a good straight line when $1/(Co^{+++})$ is plotted against time, indicating second order throughout.

In an attempt to find a function which fits the data, various ones were tried. The following equations were investigated.

$$-\frac{d(Co^{+++})}{dt} = k_1 \frac{(Co^{+++})}{(Co^{++})} + k_2 \frac{(Co^{+++})^2}{(Co^{++})} \qquad (1)$$

$$-\frac{d(Co^{+++})}{dt} = k_1 \frac{(Co^{+++})}{(Co^{++})} + k_2 \frac{(Co^{+++})^2}{(Co^{++})^2} \qquad (2)$$

$$-\frac{d(Co^{+++})}{dt} = k_1 (Co+++) + k_2 (Co^{+++})^2 \qquad (3)$$

$$-\frac{d(Co^{+++})}{dt} = k_1 (Co^{+++}) + k_2 \frac{(Co^{+++})^2}{(Co^{++})^{1/2}} \qquad (4)$$

$$-\frac{d(Co^{+++})}{dt} = k_1 (Co^{+++}) + k_2 \frac{(Co^{+++})^2}{(Co^{++})^2} \qquad (5)$$

$$-\frac{d(Co^{+++})}{dt} = k_1 (Co^{+++}) + k_2 \frac{(Co^{+++})^2}{(Co^{++})} \qquad (6)$$

With the limited data at hand, all were eliminated except (5) and (6). The cobaltic concentrations of Table IX (Figure 4) were plotted against time. Then tangents were taken from the curve (to give the values of $d(Co^{+++})/dt$ at various cobaltic concentrations) and the values thus obtained divided by the corresponding cobaltic concentrations. These are the ordinates of the points of Figure 7. The upper curve corresponds to the ratio $(Co^{+++})/(Co^{++})^2$ as abscissa, and the lower curve to the ratio $(Co^{+++})/(Co^{++})$. The former appears to give a slightly better fit to a straight line. These are equations (5) and (6) respectively. Table XI (Figure 6) gives a similar graph, equation (5) also giving the better fit. The data of Table X (Figure 5) do not give a good fit to any of these equations. It is by an analysis such as this that equations (1) to (4) were eliminated.

From such a graph k_1 is obtained as the y-intercept and k_2 as the slope of the line.

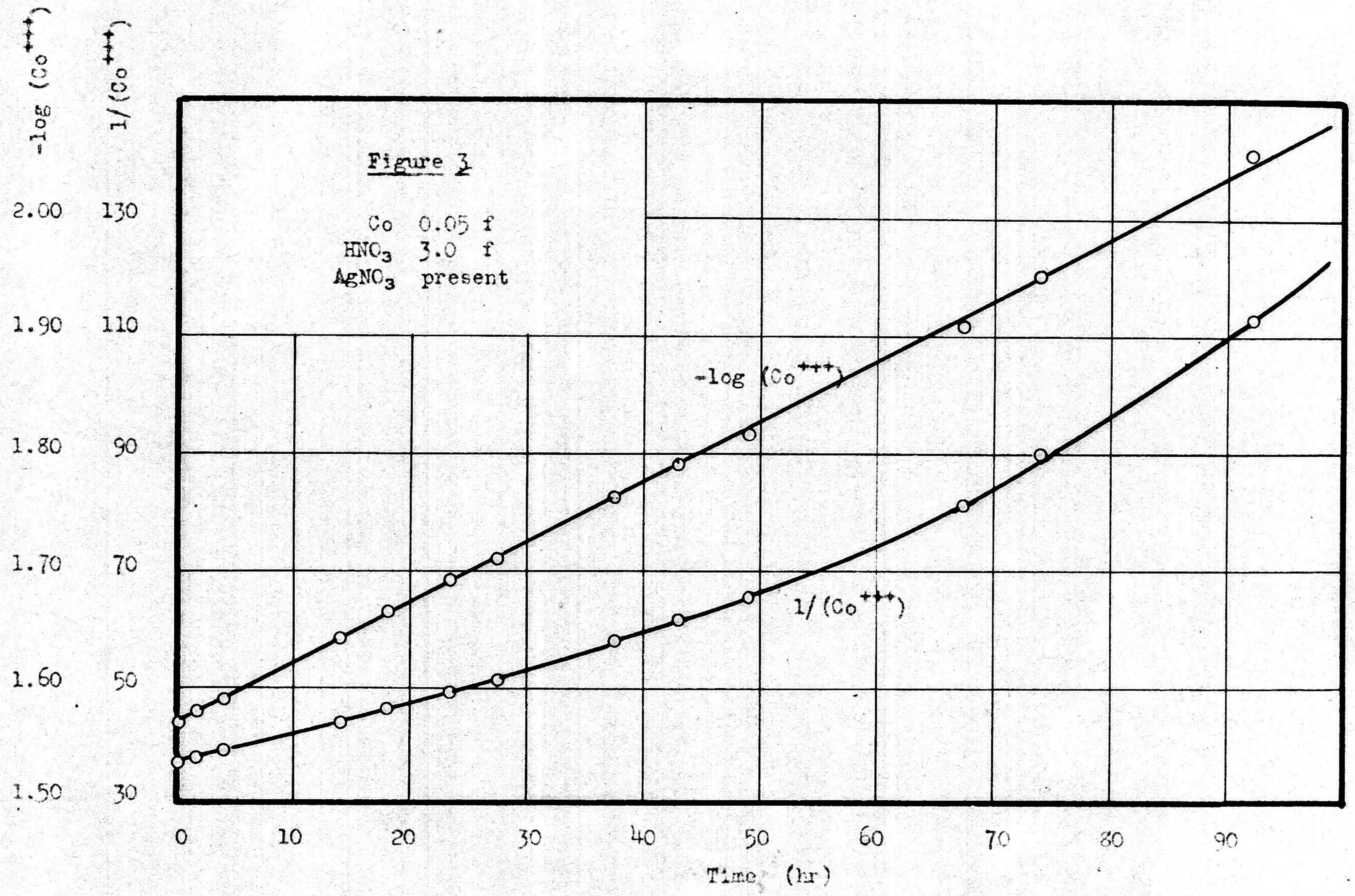

Figure 3

Co 0.05 f
HNO_3 3.0 f
$AgNO_3$ present

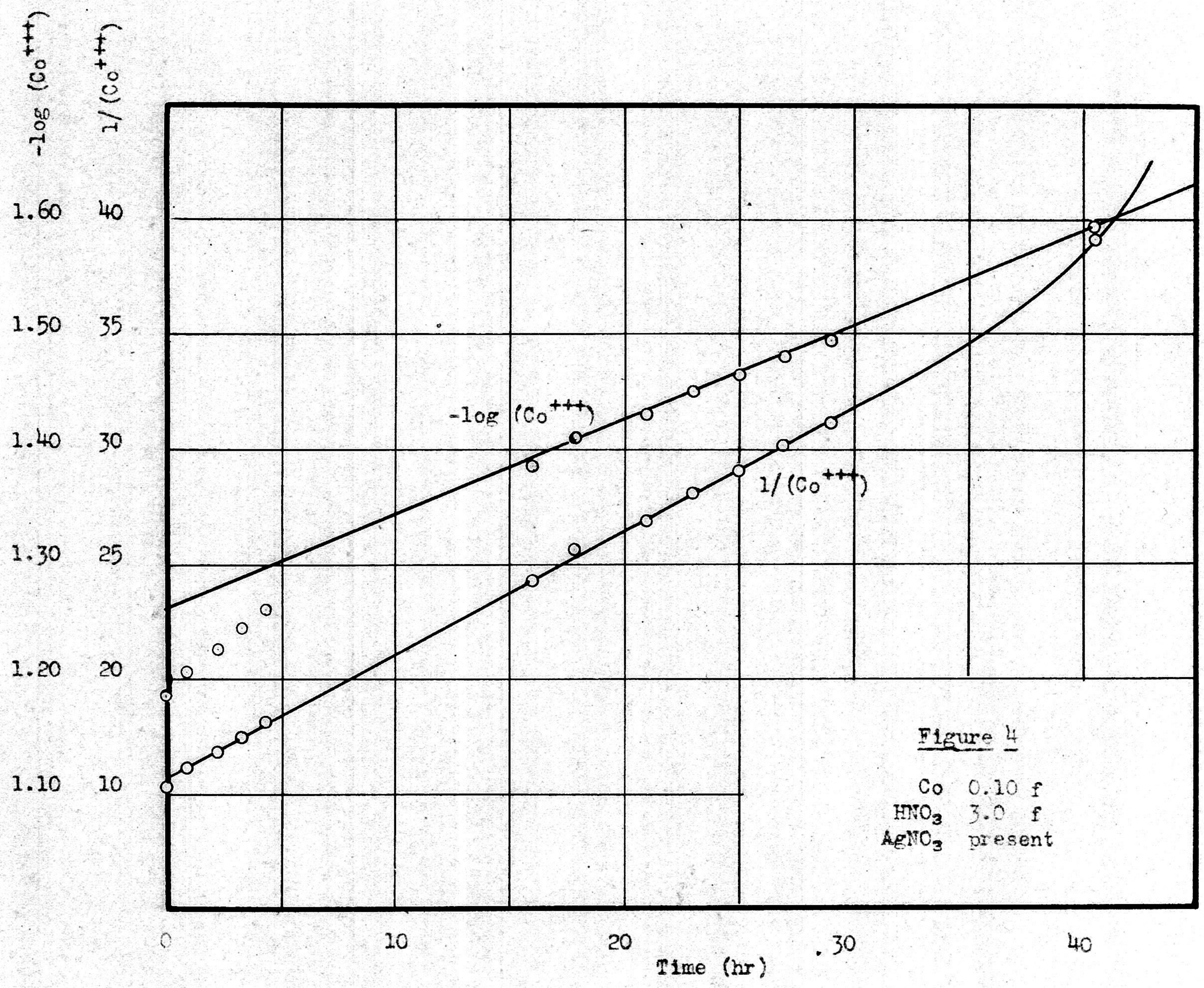

Figure 4

Co 0.10 f
HNO_3 3.0 f
$AgNO_3$ present

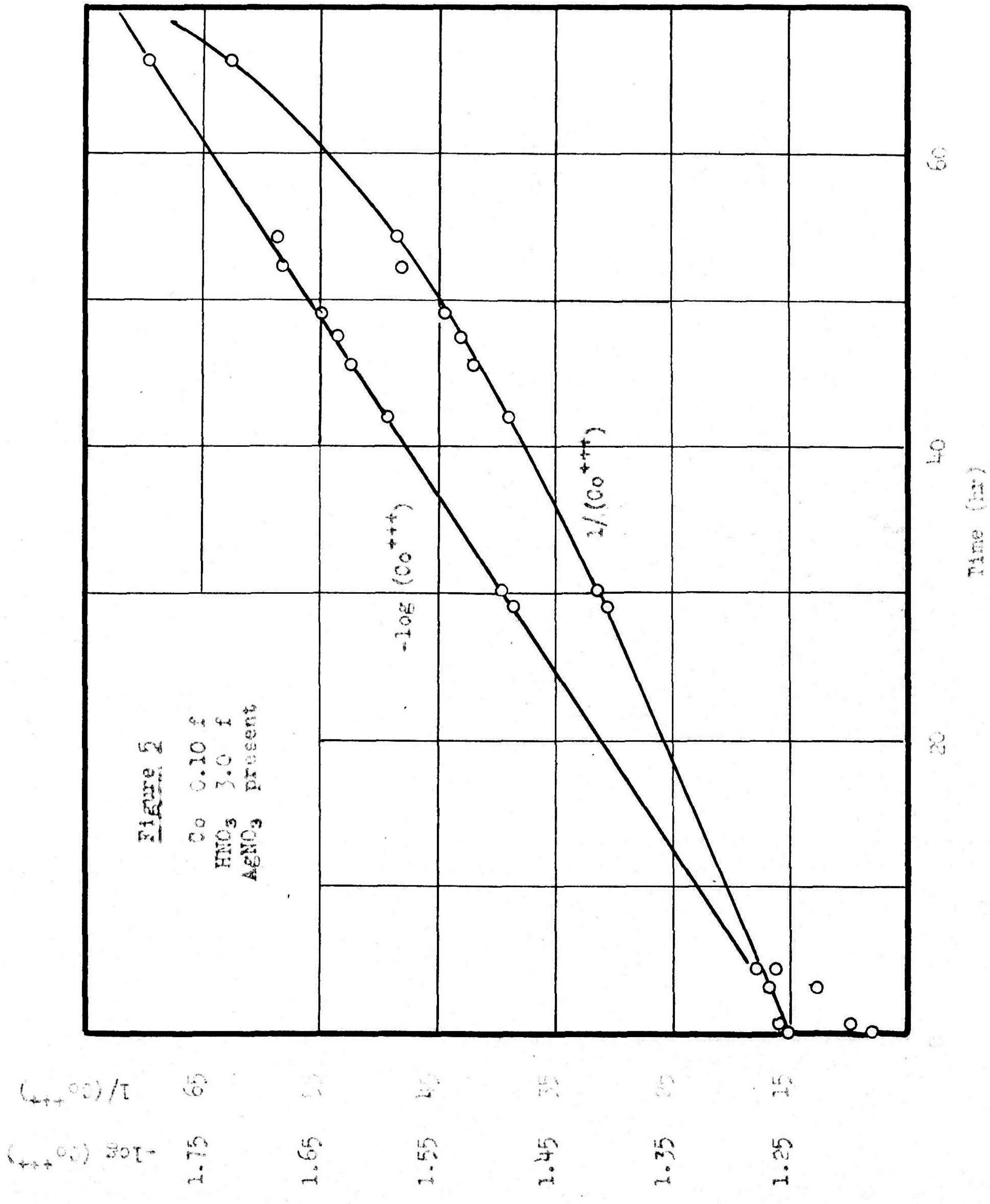

Figure 5

Co 0.10 f
HNO$_3$ 3.0 f
AgNO$_3$ present
-log (Co^{+++})
1/(Co^{+++})
Time (hr)
20
40
60
1/(Co^{+++})
65
55
45
35
25
15
-log (Co^{+++})
1.75
1.65
1.55
1.45
1.35
1.25

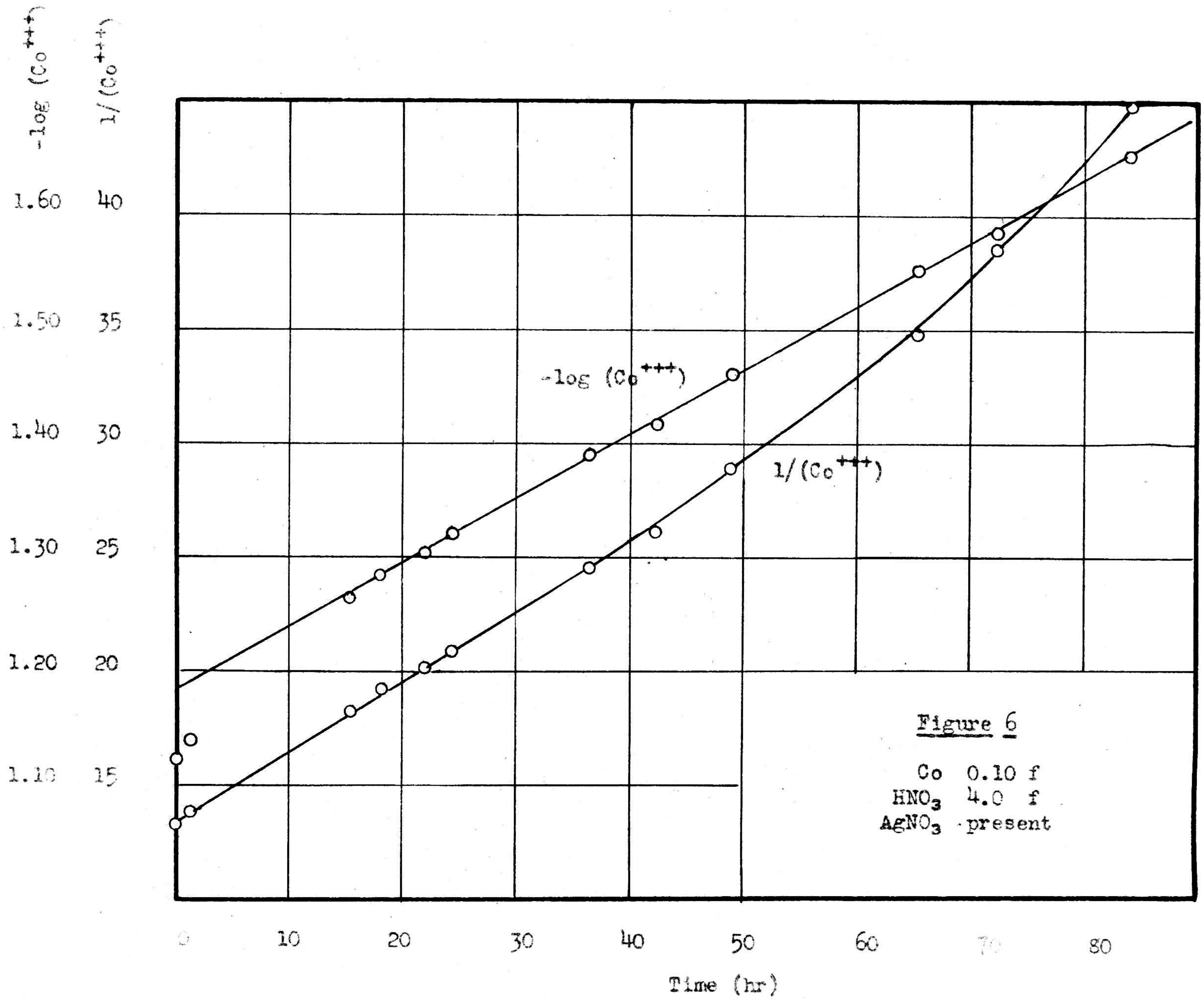

Figure 6

Co 0.10 f
HNO_3 4.0 f
$AgNO_3$ present

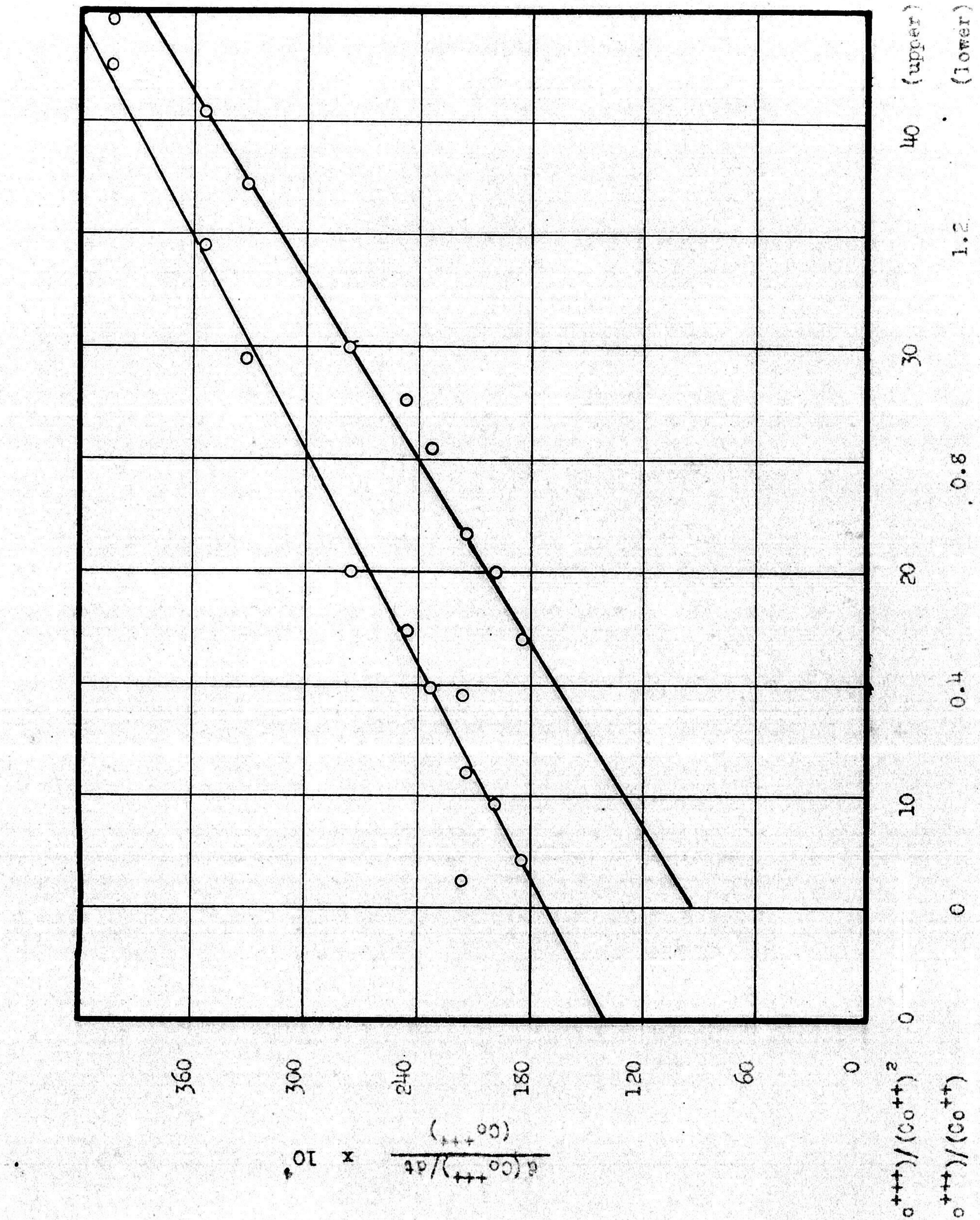
$\frac{d(Co^{+++})/dt}{(Co^{+++})} \times 10^4$
0
60
120
180
240
300
360
0
10
20
30
40
(upper)
0
0.4
0.8
1.2
(lower)
$(Co^{+++})/(Co^{++})^2$
$(Co^{+++})/(Co^{++})$

Figure I

However, equations (5) and (6) are inadequate, for if they represent the true state of affairs, then both lines should have a common y-intercept.

In order to explain the existence of the first order reaction, it seems necessary to postulate a free hydroxyl radical. The following reactions would then express the mechanism.

$$\begin{array}{lr} Co^{+++} + OH^- = Co^{++} + OH & \text{(slow)} \\ H_2O = H^+ + OH^- & \text{(rapid equilibrium)} \\ Co^{+++} + OH = Co^{++} + H^+ + \tfrac{1}{2}O_2 & \text{(rapid)} \\ \hline 2Co^{+++} + H_2O = 2Co^{++} + 2H^+ + \tfrac{1}{2}O_2 & \end{array}$$

The rate is then given by

$$-\frac{d(Co^{+++})}{dt} = k_1' (Co^{+++})(OH^-) = k_1 (Co^{+++})/(H^+).$$

Whether this is thermodynamically possible, it is difficult to say, since the free energy of formation of the hydroxyl radical in solution is not known.

The second order reaction is explained by the following mechanism.

$$\begin{array}{lr} CoO^{++} + H_2O = Co^{++} + H_2O_2 & \text{(slow)} \\ 2Co^{+++} + H_2O = CoO^{++} + Co^{++} + 2H^+ & \text{(rapid equilibrium)} \\ H_2O_2 + 2Co^{+++} = 2H^+ + 2Co^{++} + O_2 & \text{(rapid)} \\ \hline 4Co^{+++} + 2H_2O = 4Co^{+++} + 4H^+ + O_2 & \end{array}$$

Assuming that the rate is simply proportional to (CoO^{++}) and substituting for it the equilibrium expression

$$(CoO^{++}) = K\frac{(Co^{+++})^2}{(Co^{++})(H^+)^2}$$

one obtains the reaction rate expression

$$- \frac{d(Co^{+++})}{dt} = k_2' (CoO^{++}) = k_2 \frac{(Co^{+++})^2}{(Co^{++})(H^+)^2} \quad .$$

It is to be noted that there is an inverse hydrogen ion dependence in both of these rate expressions, which is in accord with experiment.

It is to be emphasized that the data are too limited to permit a satisfactory study of the kinetics of the decomposition. The main purpose of this investigation has been the determination of the cobaltous-cobaltic potential. The reaction rate study has been incidental. However, it seems safe to say that the kinetics are rather complex and a more thorough study than the present one is necessary to permit any definite conclusions to be drawn.

In view of this fact further speculations regarding the mechanism of the decomposition are omitted.

Summary

This paper describes measurements of the electromotive force of the combination comprising as one half-call a solution of cobaltous and cobaltic nitrates in 1 to 4 n nitric acid and as the other half-cell 1 to 2 n perchloric acid kept saturated with hydrogen gas. The formal oxidation potential of the reaction $Co^{III} + E^{-I} = Co^{II}$ has been computed to have values at 0°

ranging from 1.801 to 1.816 volts with increasing acid concentration. At 25° it has the value 1.842 in 3 n acid and 1.850 volts in 4 n acid. In a given acid concentration, the E^0 has been found to remain constant within 2 millivolts when the ratio Co^{II}/Co^{III} is varied several fold.

A preliminary investigation of the decomposition rate of cobaltic salts in nitric acid solution in the presence of silver nitrate has been made.

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Acknowledgment

The author wishes to express his thanks and appreciation to Dr. Noyes, under whose direction this work was carried out. He is also deeply indebted to Dr. C. D. Coryell for many helpful suggestions and criticisms and for the general interest he has shown in the work.