An unstable oxide or basic salt of tripositive silver is precipitated by electrolysis of silver perchlorate–perchloric acid solutions and also seems to form on the surface of argentic oxide treated with perchloric acid.

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Strong Oxidizing Agents in Nitric Acid Solution. III. Oxidation Potential of Cobaltous–Cobaltic Salts, with a Note on the Kinetics of the Reduction of Cobaltic Salts by Water[1]

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This study of the cobaltous–cobaltic potential is a continuation of a series of investigations on the oxidation potentials of strong oxidizing agents in nitric acid solution.[2–4] The potential was first measured by Oberer[5] and Jahn[6] in sulfuric acid solution, but no attempt was made to calculate the potentials referred to the standard molal hydrogen electrode. In the course of their extensive study of the cobaltammines, Lamb and Larson[7] measured the potential in sulfuric acid solution against a hydrogen electrode in 4 N sulfuric acid at 0 and at 16°, the potential of the reference half-cell being then measured against a normal calomel electrode through a saturated ammonium nitrate bridge.

In the present investigation, measurements were made at 0 and at 25° on cells of the type

$$\text{Pt} + \text{H}_2\ (p_{\text{H}_2}),$$
$$\text{HClO}_4\,(c'),\ \left\{\text{HNO}_3\,(c) + \begin{matrix}\text{Co}^{\text{II}}\,(c_1)\\ \text{Co}^{\text{III}}\,(c_2)\end{matrix}\right\},\ \text{Au (or Pt)} \qquad (1)$$

for which the liquid-junction potential may be calculated approximately. The acid concentration c and the ratio c_1/c_2 were varied several fold and a reliable value was obtained for the cobaltous–cobaltic potential in nitric acid solution. As the cobaltic salt is reduced by water at a measurable rate at 0°, it has been possible also to obtain information concerning the kinetics of its reduction; these results are discussed briefly.

Apparatus and Materials

Preparation and Analysis of Solutions.—A stock solution approximately 0.5 f in cobaltous nitrate was prepared by dissolving reagent-grade $Co(NO_3)_2 \cdot 6H_2O$ (nickel free) in the proper quantity of distilled water. This solution was standardized gravimetrically as cobalt sulfate. A stock solution of nitric acid was prepared by diluting C. P. nitric acid. Solutions containing cobaltous nitrate and nitric acid in different proportions were prepared by weighing out those quantities of the standardized solutions and distilled water calculated to give the desired weight-formal concentrations.

The cobalt in these stock solutions was partially converted into the tripositive form by electrolysis. The electrolytic cell used for this purpose was equipped with a platinum stirrer, which also served as the anode. The cathode, a small strip of platinum, was enclosed in a vessel made by inverting a sintered glass filter funnel which had been cut off just above the plate. This sintered plate prevented appreciable diffusion between the anode and cathode compartments. A current of about 0.8 ampere 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. The acidity of the final solution was less than that of the initial solution because of the reduction of hydrogen ions at the cathode during the electrolysis. To offset this, the initial acidity was increased from an integral value by a quantity equal to the formal concentration of total cobalt present. The increase in the acid concentration during the subsequent reduction of the cobaltic salt by water amounted in no case to more than 1.7%, and will be shown to have an entirely negligible effect upon the electromotive force of the cell.

The solutions of perchloric acid for the hydrogen half-cells were prepared by diluting the C. P. 60% acid and standardizing against a sodium hydroxide solution.

Calomel was prepared electrolytically by the method of Ellis.[8]

Tank hydrogen was purified by passing it first through a concentrated potassium hydroxide solution, then over

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(1) This problem was suggested by Professor Noyes, who directed a large part of the experimental work. After his death the investigation was continued by the junior author alone, who takes responsibility for the imperfections. The co-operation of Dr. Charles D. Coryell in the preparation of this paper for publication is appreciated.

(2) Noyes and Kossiakoff, THIS JOURNAL, **57**, 1238 (1935).

(3) Noyes and Garner, *ibid.*, **58**, 1265 (1936).

(4) Noyes and Garner, *ibid.*, **58**, 1268 (1936).

(5) Oberer, Dissertation, Zurich, 1903.

(6) Jahn, *Z. anorg. Chem.*, **60**, 292 (1908).

(7) Lamb and Larson, THIS JOURNAL, **42**, 2024 (1920).

(8) Ellis, *ibid.*, **38**, 737 (1916).

solid potassium hydroxide, and finally over an electrically heated platinum wire.

The Hydrogen Half-Cell.—The hydrogen half-cell used was similar to that described by Noyes and Garner.[8] Before entering the cell the hydrogen gas was passed through a glass coil immersed in the thermostat and then 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°.

Method of Potential Measurements.—A Student Type Leeds and Northrup potentiometer giving readings to 0.1 millivolt was used with a high-sensitivity galvanometer.

After the electrolysis had been carried on for a sufficient period, the circuit was broken and the electrodes and the hydrogen half-cell were immersed in the solution. Previously the hydrogen electrode had been checked against a 1 *f* HCl–calomel cell at the same temperature. Potential measurements were made over a period varying from twenty-five to one hundred and twenty hours, depending upon the rate of reduction of the tripositive 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 bipositive cobalt interfered with the permanganate end-point, the titration was followed potentiometrically, using a vacuum-tube voltmeter. Experiments showed that under the conditions obtaining no oxidation of ferrous ion by the nitric acid took place. The concentration of tripositive cobalt thereby determined was subtracted from the known total cobalt concentration in order to obtain that of the bipositive form. In the case of the runs made at 0°, the pipets used in withdrawing the cobalt solution had been chilled previously, as were also the flasks containing the ferrous sulfate. Potential measurements were made immediately preceding the removal of the sample and again immediately afterward. These checked to 0.1 millivolt in the experiments at 0°; at 25°, where these frequently differed by as much as 1.5 millivolts because of rapid reduction, the mean was taken as corresponding to the potential at the time of withdrawal of the sample.

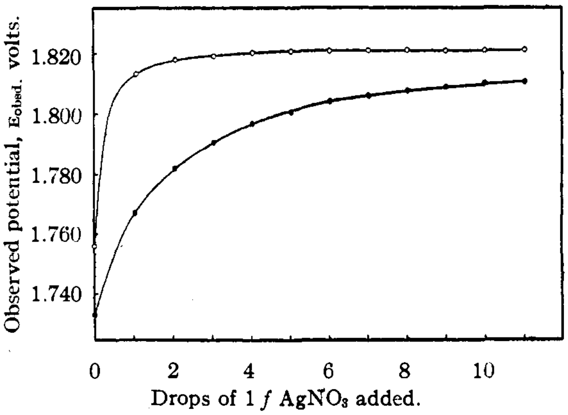

Fig. 1.—Effect of adding silver nitrate upon the observed potential: total Co, 0.1 *f*; HNO_3, 3.0 *f*; ○, gold; ●, platinum.

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

Attainment of Reproducible Potentials

Jahn[6] experienced considerable difficulty in obtaining constant and reproducible results, different electrodes prepared in the same manner giving potentials differing by several centivolts. Moreover, the time required to reach equilibrium with the solution varied from a few hours to several days. He found, however, that if an electrode were removed from a cobalt solution and the residue remaining on the electrode ignited to an oxide, reproducible results could be obtained with it. Nickel oxide was found to behave similarly. Lamb and Larson[7] likewise used a platinum foil coated with the oxide. However, they found that an uncoated gold electrode gave a higher potential.

In the present investigation the same trouble experienced by Jahn was also encountered. The difficulty lay largely in the fact that the 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 potential if it was lightly platinized before electrolysis, and the values of the formal electrode potential E^0 calculated from the observed potential for different ratios of c_1/c_2 were in good agreement. In Table I, run 1 represents measurements for which the platinum stirrer was used as the electrode. (The significance of the various potentials added to the observed one $E_{obsd.}$ to obtain E^0 will be discussed in the next section.)

Since the argentous–argentic potential is established quite readily and is of the same order of magnitude, Dr. C. D. Coryell of these laboratories suggested its use as a potential mediator. It was found that addition of a drop (1/28 ml.) of 1 *f* silver nitrate solution to about 225 ml. of the oxidized cobalt solution led to an immediate increase in the observed potential. The addition of further drops caused further increase, by smaller amounts, until after the addition of about ten drops the potential no longer rose appreciably. The same effect was observed for a gold electrode, with the difference that only about half as much silver nitrate was required to attain the maximum potential. Figure 1 shows these effects graphically. It will be noted that the maximum potential for gold is somewhat higher than that for platinum; in 1 *f* acid this difference at 0° is about 20 millivolts, while in 4 *f* acid it amounts to about 5 mv. As the tripositive cobalt decomposed, this difference increased only slightly at 0°, but at 25° it increased several millivolts. In the stronger acid a larger number of drops was required to attain the maximum potential. Small quantities of nickel nitrate were also added, but had no effect as a potential mediator.

In order to note the effect of the added silver nitrate upon E^0, run 1 (no silver present) should be compared with runs 9 and 10 (silver present); it is seen that in the presence of the potential mediator the E^0 calculated is 50 mv. higher than without it.

Before the addition of silver nitrate the potential observed with the gold electrode was usually, but not always, higher than that for platinum. In the case of 1 *f* nitric acid, the gold electrode gave a potential slightly lower than that for platinum; in 2 *f*, 3 *f*, and 4 *f* acid it was, respectively, 10, 25, and 40 higher.

It was noted that if not enough silver nitrate was added to reach the maximum potential using a platinum electrode, but yet sufficient to attain that using gold, the observed potential with platinum increased over a certain period as the tripositive cobalt was reduced, whereas the observed potential using a gold electrode decreased in accordance with the Nernst equation.

Before the addition of the silver nitrate, the observed potential with platinum was from 1 to 2 mv. lower when the solution was stirred than when it was not. After it was added, the potential with stirring was from 3 to 5 mv. higher than without stirring. In the case of the gold electrode, stirring increased the potential about 0.5 mv., both before and after the addition of the silver nitrate.

Of the values recorded, those for the gold electrode with potential mediator are believed to represent most nearly the cobaltous–cobaltic potential in nitric acid solution for the following reasons: stirring was practically without effect upon the potential; the observed potential was always higher for the gold electrode than for the platinum electrode in the presence of silver (less silver being required to give the maximum potential for gold than for platinum); and the change in $E_{obsd.}$ with change in the ratio c_1/c_2 followed the Nernst equation with gold much better than with platinum in the measurements at 25°.

The Observed and Computed Electromotive Forces

Tables I and II contain the observations on eleven cells at 0° and two at 25°. The times

TABLE I

THE OBSERVED AND CALCULATED ELECTROMOTIVE FORCES AT 0°

Gold electrode and silver nitrate used in Runs 2–11

Run 1

Pt Electrode—no $AgNO_3$ present

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.
0.0	0.65	1.739	−0.010	1.744
53.3	1.91	1.724	+ .015	1.755
54.6	1.93	1.724	+ .016	1.754
58.6	2.08	1.722	+ .017	1.755
60.8	2.14	1.720	+ .018	1.754
72.8	2.51	1.719	+ .022	1.756
80.1	2.83	1.717	+ .025	1.757
101.3	3.89	1.709	+ .032	1.757
120.9	5.18	1.703	+ .039	1.757
			Mean	1.755

HNO_3 (c) 3.0 *f* $E_L = +0.021$
($\alpha = 0.85$)
$HClO_4$ (c') 1.000 *f* $E_H = -.005$
($\alpha' = 0.803$)
Total Co = .100 *f*

Run 2

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	1.49	1.800	+0.009	1.802	0.019
2.9	2.12	1.790	+ .018	1.800	.019
5.6	2.76	1.785	+ .024	1.801	.018
18.5	5.74	1.762	+ .041	1.796	.017
20.5	6.58	1.761	+ .044	1.798	.018
			Mean	1.799	

HNO_3 (c) 1.0 *f* $E_L = -0.002$
($\alpha = 0.71$)
$HClO_4$ (c') 1.000 *f* $E_H = -.005$
($\alpha' = 0.803$)
Total Co = .0500 *f*

Run 3

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	1.48	1.798	+0.009	1.800	0.017
2.0	1.97	1.796	+ .016	1.804	.019
13.2	4.43	1.776	+ .035	1.803	.018
17.3	5.53	1.768	+ .040	1.800	.018
20.7	6.85	1.751	+ .045	1.799	.018
25.5	8.84	1.754	+ .051	1.798	.020
			Mean	1.801	

HNO_3 (c) 1.0 *f* $E_L = -0.002$
($\alpha = 0.71$)
$HClO_4$ (c') 1.000 *f* $E_H = -.005$
($\alpha' = 0.803$)
Total Co = .0500 *f*

TABLE I (*Continued*)

Run 4

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	1.41	1.797	+0.008	1.798	0.017
10.6	3.98	1.773	+ .033	1.798	.017
13.0	4.54	1.772	+ .036	1.800	.018
17.4	5.53	1.768	+ .040	1.801	.019
21.2	6.23	1.762	+ .043	1.799	.020
34.6	9.75	1.750	+ .054	1.796	.019
38.4	11.4	1.750	+ .057	1.799	.020
			Mean	1.799	

HNO_3 (c) 1.0 f E_L = −0.002
(α = 0.71)
$HClO_4$ (c') 1.000 f E_H = − .005
(α' = 0.803)
Total Co = .0500 f

Run 5

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	0.57	1.814	−0.010	1.810	0.008
2.3	.87	1.804	− .003	1.808	.008
13.6	1.99	1.780	+ .016	1.803	.008
16.1	2.22	1.778	+ .019	1.804	.008
22.1	2.70	1.773	+ .023	1.803	.008
27.4	3.36	1.769	+ .029	1.805	.009
42.6	5.09	1.757	+ .038	1.802	.008
			Mean	1.805	

HNO_3 (c) 2.0 f E_L = +0.012
(α = 0.76)
$HClO_4$ (c') 1.000 f E_H = − .005
(α' = 0.803)
Total Co = .0750 f

Run 6

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	0.97	1.798	−0.001	1.804	0.008
13.2	1.71	1.788	+ .013	1.807	.008
17.6	1.94	1.785	+ .016	1.807	.008
24.5	2.33	1.782	+ .020	1.808	.007
35.7	2.95	1.775	+ .026	1.807	.008
47.4	3.45	1.770	+ .029	1.805	.009
60.1	4.47	1.765	+ .035	1.807	.009
			Mean	1.807	

HNO_3 (c) 2.0 f E_L = +0.012
(α = 0.76)
$HClO_4$ (c') 1.000 f E_H = − .005
(α' = 0.803)
Total Co = .0750 f

Run 7

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	0.86	1.798	−0.004	1.810	0.007
1.6	.91	1.797	− .002	1.810	.007
3.9	.96	1.795	− .001	1.809	.007
14.0	1.19	1.790	+ .004	1.810	.007
18.0	1.31	1.786	+ .006	1.808	.007
23.3	1.45	1.787	+ .009	1.811	.008
27.5	1.56	1.783	+ .011	1.809	.008
37.6	1.90	1.775	+ .015	1.806	.008
43.0	2.10	1.774	+0.017	1.807	0.008
49.0	2.26	1.773	+ .019	1.807	.008
67.3	3.04	1.763	+ .026	1.805	.008
74.0	3.48	1.765	+ .029	1.810	.009
92.2	4.66	1.754	+ .036	1.806	.008
			Mean	1.808	

HNO_3 (c) 3.0 f E_L = +0.021
(α = 0.85)
$HClO_4$ (c') 1.000 f E_H = − .005
(α' = 0.803)
Total Co = .0500 f

Run 8

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	0.31	1.818	−0.028	1.806	0.007
2.8	.44	1.813	− .019	1.809	.007
4.8	.52	1.808	− .015	1.808	.007
5.9	.62	1.805	− .011	1.809	.007
18.3	1.33	1.787	+ .007	1.809	.008
20.6	1.87	1.780	+ .015	1.809	.008
24.3	1.98	1.776	+ .016	1.808	.008
			Mean	1.808	

HNO_3 (c) 3.0 f E_L = +0.021
(α = 0.85)
$HClO_4$ (c') 1.000 f E_H = − .005
(α' = 0.803)
Total Co = .0500 f

Run 9

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	0.53	1.810	−0.015	1.811	0.007
.9	.62	1.807	− .011	1.811	.007
2.3	.68	1.804	− .009	1.810	.007
3.3	.75	1.803	− .006	1.811	.007
4.3	.82	1.802	− .005	1.813	.008
16.0	1.44	1.788	+ .009	1.812	.008
17.8	1.57	1.785	+ .011	1.812	.008
21.0	1.69	1.783	+ .012	1.811	.007
23.0	1.81	1.783	+ .014	1.812	.008
24.9	1.91	1.782	+ .015	1.812	.008
27.0	2.02	1.780	+ .017	1.812	.007
29.0	2.12	1.780	+ .018	1.813	.008
40.5	2.92	1.770	+ .025	1.811	.008
			Mean	1.812	

HNO_3 (c) 3.0 f E_L = +0.021
(α = 0.85)
$HClO_4$ (c') 1.000 f E_H = − .005
(α' = 0.803)
Total Co = .100 f

Run 10

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	0.52	1.810	−0.016	1.809	0.007
.6	.58	1.809	− .013	1.812	.007
2.3	.69	1.806	− .009	1.812	.007
4.3	.83	1.800	− .005	1.811	.007
29.0	2.07	1.779	+ .017	1.811	.007
30.5	2.14	1.779	+ .018	1.812	.008
42.2	2.90	1.771	+ .025	1.812	.008
45.7	3.19	1.769	+ .027	1.811	.008

TABLE I (*Concluded*)

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
47.5	3.30	1.768	+ .028	1.811	.008
49.0	3.45	1.767	+ .029	1.811	.008
52.3	3.80	1.764	+ .032	1.811	.008
54.5	3.85	1.763	+ .032	1.811	.008
66.3	5.40	1.757	+ .040	1.812	.008
			Mean	1.811	

HNO_3 (*c*) 3.0 *f* (α = 0.85) E_L = +0.021

$HClO_4$ (*c'*) 1.000 *f* (α' = 0.803) E_H = − .005

Total Co = .100 *f*

Run 11

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.0	0.31	1.811	−0.027	1.813	0.005
1.3	.38	1.808	− .022	1.814	.004
15.4	.82	1.792	− .005	1.816	.006
18.1	.93	1.790	− .002	1.817	.004
22.0	1.01	1.787	+ .000	1.815	.004
24.5	1.09	1.785	+ .002	1.815	.004
36.7	1.45	1.778	+ .009	1.816	.004
42.3	1.61	1.776	+ .011	1.816	.004
49.0	1.89	1.772	+ .015	1.816	.005
65.3	2.51	1.765	+ .022	1.816	.005
72.2	2.84	1.762	+ .025	1.816	.005
84.2	3.50	1.757	+ .030	1.816	.005
			Mean	1.816	

HNO_3 (*c*) 4.0 *f* (α = 0.96) E_L = +0.007

$HClO_4$ (*c'*) 2.000 *f* (α' = 1.295) E_H = + .022

Total Co = 0.100 *f*

TABLE II

THE OBSERVED AND CALCULATED ELECTROMOTIVE FORCES AT 25°

Gold electrode and silver nitrate used

Run 12

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.00	3.60	1.790	+0.030	1.844	0.031
.37	5.67	1.780	+ .041	1.844	.033
.72	7.64	1.771	+ .048	1.843	.035
1.08	10.4	1.764	+ .055	1.843	.037
1.62	14.5	1.754	+ .063	1.841	.040
1.75	22.8	1.741	+ .073	1.838	.044
			Mean	1.842	

HNO_3 (*c*) 3.0 *f* (α = 0.85) E_L = 0.000

$HClO_4$ (*c'*) 2.000 *f* (α' = 1.295) E_H = + .024

Total Co = 0.100 *f*

Run 13

Time, hours	Co^{II}/Co^{III}	$E_{obsd.}$, v.	E_C, v.	E^0, v.	ΔE, v.
0.00	3.94	1.788	+0.032	1.852	0.022
.32	5.04	1.782	+ .038	1.852	.022
.70	6.45	1.776	+0.044	1.852	0.023
1.17	8.10	1.770	+ .049	1.851	.024
1.65	9.95	1.764	+ .054	1.850	.025
2.18	12.0	1.759	+ .059	1.848	.026
2.82	15.4	1.753	+ .064	1.848	.027
			Mean	1.850	

HNO_3 (*c*) 4.0 *f* (α = 0.96) E_L = +0.007

$HClO_4$ (*c'*) 2.000 *f* (α' = 1.295) E_H = + .024

Total Co = 0.100 *f*

at which potential measurements were made and the corrections to be applied to the observed potentials are also recorded.

For each run the first column gives the time in hours at which samples were withdrawn, the time of removal of the first one being taken as zero. The second column gives the ratio of the total cobaltous concentration to the total cobaltic concentration. In the third column there is recorded the observed potential $E_{obsd.}$, to which the three following corrections are made in order to obtain the formal electrode potential E^0 (for the reaction Co^{III} (1 *f*) + E^{-I} = Co^{II} (1 *f*) in nitric acid solution of the concentration prevailing):

(1) The quantity $E_C = (RT/F) \ln(c_1/c_2)$ is added in order to provide for equiformal concentrations of bipositive and tripositive cobalt. Since their activities are not known, their total concentrations (represented by c_1 and c_2, respectively) are used.

(2) 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*), where p_{H_2} is the partial pressure of the hydrogen gas in atmospheres.

(3) Finally, the quantity $E_L = (2T_H - 1)(RT/F) \ln(\alpha c/\alpha'c')$ is added to eliminate the liquid junction potential, α and α' being, respectively, the activity coefficients of nitric and perchloric acids.[9] (See ref. 2 for the assumptions underlying the use of this formula.) A test was made of the reliability of this correction: in one run in which 3 *f* nitric acid was employed, potential measurements were made first with a 1 *f* perchloric acid hydrogen electrode and then with a 2 *f* perchloric acid electrode; the average of the formal electrode potentials calculated from the potentials observed with the latter electrode

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[9] Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928); Pearce and Nelson, THIS JOURNAL, **55**, 3080 (1933).

TABLE III

VARIATION OF FORMAL ELECTRODE POTENTIAL WITH THE ACIDITY AND TEMPERATURE

Temp., °C.	0	0	0	0	0	25	25
HNO_3, *f*	1.0	2.0	3.0	3.0	4.0	3.0	4.0
Total cobalt *f*	0.05	0.075	0.05	0.10	0.10	0.10	0.10
Range 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^0, v.	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

was only 0.5 mv. higher than that obtained using the 1 *f* electrode.

The formal electrode potential E^0 (fifth column) obtained by applying these corrections to the observed potential is considered to be equal to that of the cell

$$\mathrm{Pt} + \mathrm{H_2}\,(1\text{ atm.}),\ \mathrm{H^+}\,(1\ m)\ \Bigg\|\ \left\{ \mathrm{HNO_3}\,(1\text{ to }4\ f) + \begin{matrix} \mathrm{Co^{II}}\ (1\ f) \\ \mathrm{Co^{III}}\ (1\ f) \end{matrix} \right\},\ \mathrm{Au} \qquad (2)$$

The last column labelled ΔE gives the amount by which the potential determined with a gold

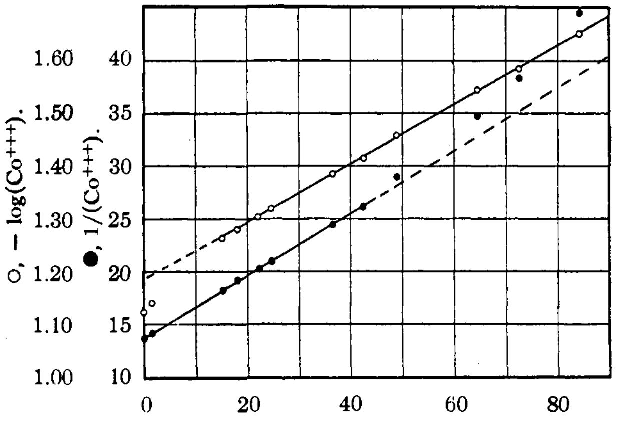

Fig. 2.—Reduction rate: total Co, 0.1 *f*; HNO_3, 4.0 *f*.

electrode exceeded that determined with a platinum electrode. In all runs except run 1, the values listed under $E_{\mathrm{obsd.}}$ and E^0 refer to those obtained for the gold electrode.

The results contained in runs 2–13 are summarized in Table III, the values recorded being those for the gold electrode in the presence of silver nitrate.

Discussion of the Results of the Potential Measurements

The increase in E^0 in going from 1 to 4 *f* acid (16 mv.) may be accounted for by the assumption of hydrolysis of the cobaltic ion to an appreciable extent in the more dilute acid (for instance, by some reaction such as $Co^{+++} + H_2O = CoOH^{++} + H^+$). The attribution of the increase to change in the activity ratio of the ions or to nitrate complex formation would correspond to an increase in activity coefficient or decrease in nitrate complex formation of the tripositive ion, relative to the bipositive, with increasing acid concentration. This effect is not great, however, corresponding approximately to a factor of 2 in cobaltic ion activity.

The values at 0° obtained by Lamb and Larson[7] from Jahn's[6] 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 by extrapolation 1.817 v. 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, because of uncertainties in eliminating the potential of the hydrogen electrode in 4 *N* sulfuric acid too much significance should not be attached to this relatively small difference of 25 or 30 mv.

The values of the decrease in free energy and in heat content at 25° for the reaction Co^{III} (1 *f*) + E^{-I} = Co^{II} (1 *f*) are as follows:

HNO_3 concn.	$-\Delta F_{298}$	$-\Delta H$
3 *f*	42,500 cal./mole	34,000 cal./mole
4 *f*	42,700	33,300
Mean	42,600	33,700

A Discussion of the Kinetics of the Reduction of Cobaltic Salts by Water

The over-all reaction for the reduction of cobaltic ion by water is

$$4Co^{+++} + 2H_2O = 4Co^{++} + 4H^+ + O_2 \qquad (3)$$

From the data in Table I certain conclusions may be drawn as to the kinetics of this reaction.

If the rate of decomposition of cobaltic ion were second order with respect to the cobaltic concentration, a plot of $1/(Co^{+++})$ against time would be linear; if the rate were first order, then a plot of $-\log(Co^{+++})$ against time would be linear. In Fig. 2 data taken from Table I, run 11, are plotted in both of these ways. It is seen that in the early stages of the run the reaction is apparently second order and, in the later stages, first order; this is characteristic of all the runs, both with and without silver. Although the type of reaction appears to remain unchanged by the presence of silver, the reduction rate is increased two or three fold. The second-order reaction seems to be more important at low cobaltous concentrations; increasing the concentration of acid slows down the rate of decomposition in both the earlier and the final stages of the runs.

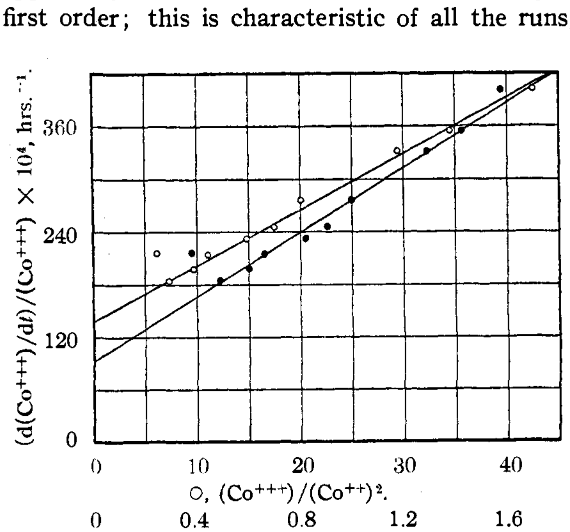

Fig. 3.—Total Co, 0.1 *f*; HNO_3, 3.0 *f*.

The rate of reduction, $-d(Co^{+++})/dt$, was determined from slopes of curves of (Co^{+++}) plotted against the time. Various kinetic expressions were then tried, although the data are not extensive enough for a complete analytic treatment. Of a number of functions tried, the following two gave the most satisfactory agreement

$$\frac{-d(Co^{+++})}{dt} = k_1\,(Co^{+++}) + k_2\,\frac{(Co^{+++})^2}{(Co^{++})^2} \quad (4)$$

$$-\frac{d(Co^{+++})}{dt} = k_1\,(Co^{+++}) + k'\,\frac{(Co^{+++})^2}{(Co^{++})} \quad (5)$$

Plots of $(-d(Co^{+++})/dt)/(Co^{+++})$ against $(Co^{+++})/(Co^{++})^2$ and $(Co^{+++})/(Co^{++})$, taken from the data for runs 9 and 11 are given as Figs. 3 and 4, respectively. In case equation (4) holds the first plot should give a straight line with an intercept on the ordinate of k_1 at $(Co^{+++}) = 0$ and slope of k_2; in case equation (5) holds, the second plot should give a straight line with the same intercept and slope k_2'. From Figs. 3 and 4 it is seen that the data fit equation (4) better. However, the data are too limited to eliminate equation (5).

The justification for this brief discussion of the reduction kinetics is the significance of the pseudo-unimolecular term in (Co^{+++}). This indicates the transfer of only one electron in the reduction if Co^{++} be the first product of the slow step, which demands the existence of some odd molecular species as an intermediate, such as free hydroxyl radical. An alternative explanation is that the Co^{+++} is reduced in the slow step by water to give unipositive Co^{+} and H_2O_2, which are both then rapidly oxidized by excess Co^{+++}.

A reaction bimolecular in Co^{+++} with inverse Co^{++} dependence could be explained by the presence of tetrapositive cobalt or its hydrolysis products in equilibrium with the tripositive form, and reaction of this with water to give Co^{++} and H_2O_2, analogous to the manner in which argentic silver is reduced.[10] This explanation, however, is compatible only with equation (5) above; a similar reasonable interpretation of equation (4) has not suggested itself.

The kinetic reactivity of cobaltic salts appears to be considerably less than that of argentic salts. 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, and after half an

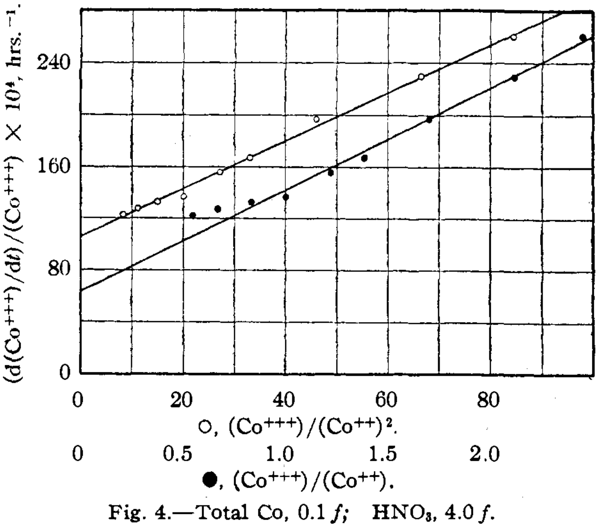

Fig. 4.—Total Co, 0.1 *f*; HNO_3, 4.0 *f*.

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[10] Noyes, Coryell, Stitt and Kossiakoff, THIS JOURNAL, **59**, 1316 (1937).

hour the color of permanganate is apparent; if, however, a drop of silver nitrate solution is added after the two solutions are mixed the color of permanganate appears immediately. The color of a solution of chromic and cobaltic salts appears after twenty-four hours 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 half an hour the color is almost that of pure dichromate.

Summary

Measurements have been described above of the electromotive force of the system comprising as one half-cell a gold electrode immersed in a solution of cobaltous and cobaltic nitrates in 1 to 4 *f* nitric acid, and as the other half-cell a hydrogen electrode in 1 or 2 *f* perchloric acid. Conditions for the attainment of reproducible potentials have been discussed. The formal oxidation potential for the reaction $Co^{III} + E^{-I} = Co^{II}$ has been computed to have values at 0° ranging from **1.800** volts in 1 *f* nitric acid to 1.**816** volts in 4 *f* nitric acid, and values at 25° of 1.**842** volts in 3 *f* acid and **1.850** volts in 4 *f* acid. Values of the decrease in free energy and heat content for the reaction have also been presented.

A brief discussion of the rate of reduction of cobaltic salts by water in nitric acid solution in the presence of silver nitrate has been given.

PASADENA, CALIF. RECEIVED APRIL 26, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Dipole Moments of Hydrazides

BY PAUL R. FREY[1] AND E. C. GILBERT

On the basis of a postulated unbalanced electronic structure for hydrazine it was predicted a number of years ago by Stieglitz that certain types of hydrazine derivatives should undergo rearrangement of the so-called Stieglitz–Lossen type. The correctness of this prediction has been demonstrated by Stieglitz and his students[2] and by independent work in this Laboratory.[3]

In the earlier work[2] it was proved that benzoyl hydrazide, *sym*-dibenzoyl hydrazide, and azodibenzoyl undergo rearrangement, and in the later work α-benzoyl-β-*p*-chlorobenzoyl hydrazide, α-benzoyl-β-*p*-toluyl hydrazide and α-benzoyl-β-*p*-nitrobenzoyl hydrazide were found to react similarly. In the case of the unsymmetrical derivatives the products of the reaction seemed definitely to indicate that substituents in the benzoyl group affect the electronic charge on the nitrogens, rendering one or the other more "positive" depending upon the substituent.

Recently the dipole moments of hydrazine and a number of its simple derivatives have been measured[4] and molecular structure calculated from quantum mechanical considerations.[5] These measurements confirm the correctness of the early postulate that hydrazine and its derivatives possess an unbalanced electronic configuration. Furthermore, the ingenious shift in molecular orientation used by Ulich, Peisker and Audrieth[4] to explain their dipole measurements for substituted hydrazines seems to offer a possible explanation for the results obtained in rearrangements in this Laboratory.[3]

The present work was begun before the supporting results of the other investigators were available.[4,5] It had for its purpose a study of the dipole moments of those hydrazides which were known to undergo rearrangement in the hope of finding some fundamental explanation for their behavior. The experimental work presented considerable difficulty because of the relative insolubility of the compounds in non-polar solvents, necessitating special care and the use of somewhat lower concentrations than those usually employed.

Experimental Part

Apparatus.—The heterodyne beat method[6] was used to measure dielectric constants. The two oscillators employed type 112-A tubes as a source of oscillation and were coupled to a three-tube resistance-coupled amplifier using

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[1] This paper is taken in part from the Ph.D. dissertation of Paul R. Frey, Oregon State College, June, 1936.

[2] Stieglitz and Senior, THIS JOURNAL, **38**, 2727 (1916); Stieglitz and Brown, *ibid.*, **44**, 1270 (1922); Gilbert, Abstract of Theses, University of Chicago, Science Series, 1, 177 (1923).

[3] Gilbert, THIS JOURNAL, **49**, 286 (1927).

[4] Audrieth, Nespital and Ulich, *ibid.*, **55**, 673 (1933); Ulich, Peisker and Audrieth, *Ber.*, **68B**, 1677 (1935).

[5] Penney and Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934).

[6] Williams, THIS JOURNAL, **52**, 1831 (1930).