This shows that compared with cobaltous hexammine and with the other metal ammines, cobaltic hexammine (and similarly the other cobaltic ammines) are extremely stable.

Summary.

1. The oxidation potentials of aqueous solutions of 6 representative cobaltic ammines have been measured in 3.265 *M* ammonium hydroxide solution. From these potentials the concentrations of simple cobaltic ions in these solutions have been computed and the relative stabilities of the ammines thus ascertained. Their stability is very great as compared with other metal ammines. The 6 ammines, arranged in the order of stability, are as follows: Aquo-pentammine cobaltic chloride, diaquo-tetrammine cobaltic chloride, 1,2-dinitro-tetrammine cobaltic chloride, nitro-pentammine cobaltic chloride, hexammine cobaltic chloride, 1,6-dinitro-tetrammine cobaltic chloride.

2. Incidentally:

(*a*) The potentials of the cobalt-cobaltous electrode in cobaltic chloride solution and in ammoniacal cobaltic chloride solutions have been measured. From them the formula of the cobaltous ammine ion in the presence of excess ammonia has been shown to be $Co^{++}(NH_3)_6$ and the equilibrium constant for its dissociation into ammonia and simple cobaltous ions has been computed.

(*b*) The cobaltous-cobaltic potential has been determined at 16° and redetermined at 0°. From them the potential at 25° has been obtained by interpolation.

(*c*) The potential of the hydrogen electrode in 2 *M* sulfuric acid has been measured at 0° and at 16° C. against a calomel electrode.

CAMBRIDGE 38, MASS.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE DETERMINATION OF POTASSIUM AS PERCHLORATE. III.

BY GREGORY P. BAXTER AND FRANK E. RUPERT.

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In recent papers Baxter and Kobayashi[1] have proposed certain modifications in the procedure for the determination of potassium as perchlorate and have supported the use of absolute ethyl alcohol containing perchloric acid and saturated with potassium perchlorate as the washing liquid, after the initial extraction of sodium perchlorate has been carried out with alcohol containing perchloric acid only. They have also advocated working at freezing temperature and found that at least one solution of the precipitate in water and evaporation to dryness with a slight

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[1] Baxter and Kobayashi, THIS JOURNAL, 39, 249 (1917); 42, 735 (1920).

excess of perchloric acid is necessary to eliminate inclusion of sodium salt by the potassium salt.

As substitutes for ethyl alcohol we have investigated in a similar fashion methyl alcohol, and ethyl alcohol denatured with 5% of methyl alcohol.

Potassium perchlorate was purified for the experimental work by 2 crystallizations from water. Fairly pure *perchloric acid* was twice distilled under reduced pressure in an all-glass apparatus. By determining the specific gravity of the distillate it was found to contain 56.3% of acid. After evaporation in a weighed platinum crucible 30 cc. left a residue of 0.5 mg. wholly soluble in a few cc. of alcohol. *Sodium perchlorate* was made from the distilled perchloric acid and twice crystallized sodium carbonate. After the solution had been evaporated to dryness, the residue was dissolved in absolute ethyl alcohol containing 0.1% of perchloric acid, and the solution was filtered through a platinum sponge crucible. The operations of evaporation to dryness, solution in alcohol and filtration were then repeated. This last solution was evaporated to dryness and the residue was dissolved in water to make a 10% solution, from which suitable quantities could be measured out for separate experiments. *Ethyl* and *methyl alcohols* were dehydrated over lime and distilled through a Hempel column.

First, approximate determinations of the solubility of potassium perchlorate were made in methyl alcohol, and in ethyl alcohol denatured with 5% of methyl alcohol, both with and without the addition of perchloric acid. A large excess of finely powdered potassium perchlorate was placed in 100-cc. flasks, which were filled with the alcoholic solution and frequently shaken by hand while kept at the temperature in question by immersion in an ice-bath or in a thermostat maintained at 20°. The solutions were filtered through platinum sponge crucibles into weighed platinum dishes in which they were evaporated to dryness over an electric stove. The residues were heated to about 200° before being weighed.

Since the solubility in methyl alcohol was found to be many times that in the denatured alcohol, while the latter differs very little from pure ethyl alcohol in its effect, no further experiments with methyl alcohol were made.

TABLE I.

Grams of $KClO_4$ in 100 cc. of Methyl Alcohol.

$HClO_4$. %.	0°.	20°.
0.0	0.0497	0.0745
0.0	0.0492	0.0749
0.4	..	0.0216
0.4	..	0.0216
0.8	0.0090	0.0176
0.8	0.0096	0.0178
2.4	..	0.0120
2.4	..	0.0123

TABLE II.

Grams of $KClO_4$ in 100 cc. of Denatured Alcohol.

$HClO_4$. %.	0°.	20°.
0.0	0.0086	0.0120
0.0	0.0086	0.0114
0.1	0.0022	0.0033
0.1	0.0021	0.0032
0.2	0.0022	0.0030
0.2	0.0021	0.0029
0.4	0.0018	0.0028
0.4	0.0019	0.0028
0.8	..	0.0025
0.8	..	0.0026

Blank experiments for the recovery of potassium perchlorate in the presence of sodium perchlorate were carried out as in the work by Baxter and Kobayashi, except that denatured alcohol was substituted for ethyl alcohol. The procedure was as follows.

An exactly weighed quantity of dry potassium perchlorate together with an approximately weighed portion of sodium perchlorate was dissolved in water in a platinum dish, and the solution was evaporated to dryness with a small quantity of perchloric acid. The residue was extracted with 20 cc. of denatured alcohol containing 0.2% of perchloric acid and was washed with two 5 cc. portions of the same solution, which is designated "A" in the tables. The first extract and rinsings were poured through a weighed platinum-sponge crucible. Next the potassium perchlorate was dissolved in water and the solution was evaporated to dryness with a small quantity of perchloric acid and the residue was extracted, washed by decantation and transferred to the original platinum-sponge crucible with denatured alcohol containing 0.2% perchloric acid and saturated with potassium perchlorate.[1] This solution is designated "W" in the tables. In the experiments recorded in Table III the operations were performed at 0°, while the experiments recorded in Table IV were performed at about 20°.

Since Expts. 3 to 9 and 14 to 19 show positive errors in nearly every case, in Expts. 10 to 13 and 20 to 23, in order to eliminate residual inclusion of sodium salt, the second precipitate of potassium perchlorate, after being rinsed, was dissolved in dil. perchloric acid and the solution evaporated to dryness still again before the final extraction and transfer to the crucible. The later modification had little if any effect.

The following experiments indicate that ethyl alcohol denatured with 5% of methyl alcohol may safely be substituted for ethyl alcohol in the washing of potassium perchlorate.

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[1] Made by dissolving the necessary quantity of potassium perchlorate in warm conc. perchloric acid and adding the solution to the alcohol.

TABLE III.

Expt.	First extract. Cc.	Washings. Cc.	At 0° $NaClO_4$ taken. G.	$KClO_4$ taken. G.	$KClO_4$ found. G.	Error. G.
1.....	A 20 + 5 + 5	W 90	0.0	0.3013	0.3011	−0.0002
2.....	A 20 + 5 + 5	W 90	0.0	0.3451	0.3449	−0.0002
3.....	A 20 + 5 + 5	W 75	0.5	0.3021	0.3027	+0.0006
4.....	A 20 + 5 + 5	W 75	0.5	0.3446	0.3450	+0.0004
5.....	A 20 + 5 + 5	W 75	0.1	0.3002	0.3005	+0.0003
6.....	A 20 + 5 + 5	W 75	0.1	0.3326	0.3329	+0.0003
7.....	A 20 + 5 + 5	W 75	0.3	0.2999	0.3002	+0.0003
8.....	A 20 + 5 + 5	W 75	1.0	0.3029	0.3033	+0.0004
9.....	A 20 + 5 + 5	W 75	1.0	0.3164	0.3168	+0.0004
10.....	A 20 + 5 + 5	W 90	0.5	0.3018	0.3019	+0.0001
11.....	A 20 + 5 + 5	W 90	0.5	0.3183	0.3183	+0.0000
12.....	A 20 + 5 + 5	W 90	1.0	0.3002	0.3004	+0.0002
13.....	A 20 + 5 + 5	W 90	1.0	0.3188	0.3189	+0.0001

TABLE IV.

			At 20°.			
14.....	A 20 + 5 + 5	W 75	0.5	0.3003	0.3007	+0.0004
15.....	A 20 + 5 + 5	W 75	0.5	0.3083	0.3084	+0.0001
16.....	A 20 + 5 + 5	W 75	0.1	0.2984	0.2983	−0.0001
17.....	A 20 + 5 + 5	W 75	0.1	0.3052	0.3053	+0.0001
18.....	A 20 + 5 + 5	W 75	1.0	0.3008	0.3010	+0.0002
19.....	A 20 + 5 + 5	W 80	1.0	0.3056	0.3059	+0.0003
20.....	A 20 + 5 + 5	W 95	0.5	0.3017	0.3019	+0.0002
21.....	A 20 + 5 + 5	W 100	0.5	0.3091	0.3093	+0.0002
22.....	A 20 + 5 + 5	W 100	1.0	0.3020	0.3022	+0.0002
23.....	A 20 + 5 + 5	W 100	1.0	0.3096	0.3099	+0.0003

It also is evident that in the procedure described the temperature is unimportant, if the washing liquid employed after the initial extraction is previously saturated with the precipitate.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE.]

GELATIN AS AN EMULSIFYING AGENT.

BY HARRY N. HOLMES AND WM. C. CHILD.

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Various theories of the action of emulsifying agents have been offered. Plateau[1] and Quincke[2] considered the lowering of surface tension of one of the 2 liquids as the most important factor, with viscosity next. Pickering[3] believed that a droplet covering of small insoluble solid particles was a vital factor. He demonstrated his theory by the use of basic ferrous and cupric sulfates. Martin Fischer[4] states that solvated sub-

[1] Plateau, *Ann. Physik.*, **141**, 44 (1870).

[2] Quincke, *ibid.*, **271**, 580 (1888).

[3] Pickering, *J. Chem. Soc.*, **91**, 2001 (1907).

[4] Fischer, *Science*, **43**, 468 (1916); "Fats and Fatty Degeneration," Wiley and Sons (1917).