[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE PERCHLORATES OF THE ALKALI AND ALKALINE EARTH METALS AND AMMONIUM. THEIR SOLUBILITY IN WATER AND OTHER SOLVENTS[1]

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The work done in connection with this paper deals with the perchlorates of barium, strontium, calcium, magnesium, lithium, sodium, potassium, rubidium, cesium and ammonium. Solubilities of the anhydrous perchlorates at 25° were determined in water and in anhydrous methyl, ethyl, *n*-propyl, *iso*- and *n*-butyl alcohols, ether, acetone and ethyl acetate. The solubility of lithium perchlorate trihydrate was also determined in the above solvents. In the study of these perchlorates a careful search was made for new hydrates and into the conditions for their preparation.

Historical

On account of lack of space, no description will be given of previous work on the perchlorates of these metals, but the references only will be listed as a footnote.[2]

Preparation of Materials

Perchloric Acid.—This was prepared by the method of Willard[3] and was twice distilled under a pressure of 5–15 mm. It contained 70–72.5% of perchloric acid and was free from non-volatile matter.

[1] From a thesis presented by G. Frederick Smith to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (*a*) Serrulas, *Ann. chim. phys.*, [2] **46**, 297 (1831) (K, Na, Ba, Sr, Ca, Mg, Al, Li, NH_4, Zn, Cd, Mn, Fe, Cu, Pb, Hg, Ag); Marignac, *Jahresber.*, **1855**, 342, (Ba); Potilitzin, *J. Russ. Phys. Chem. Soc.*, **19**, I, 339 (1887) (Ba); **20**, I, 541 (1888) (Li); **21**, I, 258 (1889) (Na); Wyrouboff, *Z. Kryst. Mineral.*, **10**, 625 (1885) (Li); Richards and Willard, THIS JOURNAL, **32**, 4 (1910) (Li); Richards and Cox, *ibid.*, **36**, 819 (1914) (Li); Weinland and Ensgraber, *Z. anorg. Chem.*, **84**, 370 (1914) (Mg, Al, Fe, Cr); Willard and Smith, *ibid.*, **44**, 2255 (1922) (Mg); Carlson, *Festsk. Stockholm*, **1911**, 262 (Ba, NH_4, Cs, K, Rb, Na, Tl); Louguinine, *Ann.*, **121**, 123 (1862) (Rb); Erdmann, *Arch. Pharm.*, **232**, 23 (1894) (Rb); Calzolari, *Acc. Sci. Med. Ferrara*, **85**, 150 (1911) (K, Rb, Cs); Thin and Cumming, *J. Chem. Soc.*, **107**, 361 (1915) (K, NH_4); Schlösing, *Compt. rend.*, **73**, 1269 (1871) (K, NH_4); Muir, *Chem. News*, **33**, 15 (1876) (K); Hutstein, *Arch. Pharm.*, [2] **65**, 159 (1851) (K); Wenze, *Z. angew. Chem.*, **23**, 691 (1891) (K); Noyes and Sammet, *Z. physik. Chem.*, **43**, 530 (1903) (K); Rothmund, *ibid.*, **69**, 538 (1909) (K); Noyes and Boggs, THIS JOURNAL, **33**, 1650 (1911) (K); Naumann, *Ber.*, **42**, 3790 (1909); **43**, 314 (1910) (K); Baxter and Kobyaski, THIS JOURNAL, **39**, 249 (1917); **42**, 735 (1920) (K); Baxter and Rupert, *ibid.*, **42**, 2046 (1920) (K); Mitscherlich, *Ann. Phys. Chem.*, **25**, 300 (1833) (NH_4); Hofmann, Höbold and Quoos, *Ann.*, **386**, 304 (1912) (NH_4); Eidmann, *Chem. Centr.*, **1899**, II, 1014 (NH_4).

[3] Willard, THIS JOURNAL, **34**, 1480 (1912).

Calcium Perchlorate.—Pure calcium nitrate was twice recrystallized, using centrifugal drainage, and converted into the perchlorate by evaporation with excess of perchloric acid. The excess of acid was neutralized by pure calcium carbonate, prepared from the purified nitrate by precipitation with pure ammonium carbonate. The solution was centrifuged until a clear supernatant liquid could be decanted. This was then crystallized.

Calcium perchlorate contains 4 molecules of water of crystallization and melts below 100°. It was heated at a gradually increasing temperature until all crystal water was expelled and finally dried to constant weight at 250°. It was perfectly stable at 260–270°.

Some of the crystals were dried to constant weight in a desiccator over the anhydrous salt. Upon further heating to 250° the salt lost 23.11% of water; the theoretical value for the tetrahydrate is 23.15%.

Strontium Perchlorate.—Pure strontium nitrate was twice recrystallized and converted into perchlorate in the manner just described for the calcium salt. It was dried to constant weight at 250°.

When crystallized at about 0°, strontium perchlorate apparently contains 4 molecules of water, although the data on this point are only approximate. At about 25° a dihydrate is obtained (found, 11.19% of water; calc., 11.17%) and the crystals formed above 40° after drying for several days over the anhydrous salt contained 8.65% of water, corresponding to the formula, $3Sr(ClO_4)_2.2H_2O$, which requires 8.62%. The transition point of $3Sr(ClO_4)_2.2H_2O$ to $Sr(ClO_4)_2.2H_2O$ was found to be approximately 37°. So pronounced is the tendency of the former salt to form supersaturated solutions that its solubility in water at 25° was determined without any separation of the stable phase.

When tristrontium-perchlorate dihydrate was dried over the anhydrous salt for 30 days, it showed a water content of 7.77% as compared with the original 8.62%. This indicates the possible existence of a monohydrate.

Barium Perchlorate.—Very pure barium chloride was evaporated with an excess of perchloric acid and the barium perchlorate thus obtained was recrystallized twice at about 25°. This removed all excess of acid. The crystals dried to constant weight over the anhydrous salt contained 5.04% of water; the dihydrate requires 5.08%. Other investigators have obtained the trihydrate by recrystallization from water. When the crystals are dried over sulfuric acid the monohydrate is obtained. The mono- and dihydrates when exposed to moist air until constant in weight, formed the trihydrate (found, 13.80% of water; calc., 13.85%). The latter, when heated gradually to 250° in a current of dry air, lost all of its water without melting. A sample of the anhydrous salt thus prepared, when heated at 400° for 2 hours, gave up no water to a weighed phosphorus pentoxide tube. It then contained 2.89% of barium chloride, resulting from the slight decomposition at this temperature.

Magnesium Perchlorate.—The preparation and properties of this salt have been described in a previous paper.[4]

Lithium Perchlorate.—The preparation of the trihydrate and anhydrous salt have been described in a previous paper.[5]

Sodium Perchlorate.—The preparation of this salt was described in a previous paper.[5]

Potassium Perchlorate.—Very pure potassium carbonate was neutralized with perchloric acid, recrystallized and dried at 250°.

Rubidium Perchlorate.—The rubidium nitrate available contained cesium which was removed in the following manner. To 40 g. of the nitrate dissolved in 300 cc. of water was added silicotungstic acid in excess of that required to precipitate the cesium,[6] and the precipitate of cesium with some rubidium silicotungstate was filtered off, ammonium carbonate was added, and the solution boiled to precipitate the silica, which was filtered off. The solution was acidified and evaporated to dryness to separate the tungstic acid. The residue was extracted with water, filtered, and the solution evaporated with an excess of perchloric acid. The rubidium perchlorate thus obtained was recrystallized and dried at 250°. It gave no spectroscopic indication of cesium.

Cesium Perchlorate.—A very pure sample of cesium chloride prepared from pollucite was kindly furnished by Mr. E. O. Scott. It was converted to perchlorate by evaporation with excess of perchloric acid, recrystallized and dried at 250°.

Ammonium Perchlorate.—Ammonia gas, from the action of sodium hydroxide on pure ammonium chloride, was passed into dil. perchloric acid. The salt was recrystallized and dried at 110°, at which temperature it showed constant weight.

The Purification and Dehydration of Solvents.—Some of the alcohols, particularly *n*-propyl alcohol, were difficult to obtain pure, even when purchased from reliable sources. Acetone was purified by the bisulfite process.

A 90cm. side-drained, distillation column with 6 bulbs was used in fractionating the solvents; and most of the boiling points were determined by inserting through the center of the column a standardized thermometer, the entire length of which was surrounded by the vapors of the distilling liquid. This avoided stem corrections. The table of Young[7] was used in correcting boiling points for changes in barometric pressure. The most reliable physical constants in the literature are probably those by Young[8] and Brunel, Crenshaw and Tobin.[9] From the data obtained later it is

[4] Willard and Smith, THIS JOURNAL, **44**, 2255 (1922).

[5] Willard and Smith, *ibid.*, **44**, 2816 (1922).

[6] Godeffroy, *Ber.*, **9**, 1363 (1876).

[7] Young, *J. Chem. Soc.*, **81**, 777 (1902).

[8] Young, *Proc. Dublin Phil. Soc.*, [2] **12**, 374 (1910).

[9] Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 561 (1921).

probable that slight amounts of organic impurities, especially those similar in nature to the solvent used, would have no appreciable effect on the solubility results, but even traces of water have a large influence. Accordingly, particular care was used in dehydrating the solvents. The alcohols were refluxed with metallic calcium, the ethyl ether and ethyl acetate with phosphorus pentoxide, and the acetone with powdered potassium hydroxide. The physical constants of the solvents are given in Table I.

TABLE I
PHYSICAL CONSTANTS OF THE SOLVENTS

Solvent number	Solvent	B. p. range ° C.	Mean b. p. ° C.	Density 25°/4° corrected to a vacuum
1	Methyl alcohol	64.77–64.89	64.88	0.78705
2	Methyl alcohol	64.89–65.09	64.99	0.78735
3	Ethyl alcohol	78.29–78.31	78.30	0.78517
4	Ethyl alcohol	78.29–78.31	78.30	0.78515
5	*n*-Propyl alcohol	97.5 –98.0	97.75	0.7989
6	*n*-Propyl alcohol	96.95–97.0	96.98	0.8026
7	*n*-Propyl alcohol	97.13–97.17	97.15	0.8009
8	*n*-Propyl alcohol	98.0 –98.2	98.1	0.7993
9	*iso*Butyl alcohol	Standard thermometer not used	...	0.79807
10	*n*-Butyl alcohol	116.15–116.65	116.40	0.8059
11	Acetone	56.16–56.51	56.34	0.7852
12	Acetone	.....	57.05	0.7864
13	Ethyl acetate	77.14–77.16	77.15	0.8945
14	Ethyl acetate	75.9 –78.7	77.3	0.8923
15	Ether "over sodium" (imported)	Not determined	...	0.7081

The perchlorates, the solubilities of which were determined in each solvent, are given in Table II.

TABLE II
PERCHLORATES AND SOLVENTS USED

Solvent No.	
1	Rb, Na, K, Ba, Sr, Ca, Mg, Li.
2	(NH_4), Cs.
3	Cs, Sr, Ba, Ca, Li.
4	Na, K, Rb, Mg, (NH_4).
5	Rb, Sr, Mg, Ba, Ca, Li.
6	Na.
7	K.
8	(NH_4), Cs.
9	Rb, Cs, Na, K, Sr, Mg, Ba, Ca, (NH_4), Li.
10	Rb, Cs, Na, K, Sr, Mg, Ba, Ca, (NH_4), Li.
11	Rb, Cs, Na, K, Sr, Ba, Ca, (NH_4), Li.
12	Ba.
13	Rb, Cs, Na, K, Sr, Mg, Ca, (NH_4), Li.
14	Ba.
15	Rb, Cs, Na, K, Ba, Sr, Ca, (NH_4), Li, Mg.

Apparatus and Methods

The usual procedure involved in the ordinary type of solubility determination could not be followed in this work. Most of the perchlorates dealt with were so extremely soluble in all the solvents used that sirupy solutions resulted. It was found that some equilibria between solute and solvent required that the solution be agitated for periods varying from 48 hours to more than 150 hours, and approaching the equilibrium from either side did not alter the circumstances. In many cases it required a week or more for the excess of solid to settle out so that a clear solution could be drawn off. In any case filtration was impracticable.

The temperature coefficient of solubility was often so high that it was almost impossible to estimate the requisite amount of the solute for a given volume of the solution. A solution a few degrees above 25° would often become so pasty upon cooling it to 25° that it would no longer flow.

These conditions demanded a thermostat constant to within 0.01° of the chosen temperature and capable of operation over long periods of time. A thermostat was made which satisfied these requirements in every way. The temperature, as indicated by a Beckmann thermometer, "set" by comparison with a thermometer certified by the Bureau of Standards, never varied more than 0.01°.

The method of procedure employed for making a solubility determination was as follows. The solution of the perchlorate was prepared by charging a dry 50cc. Erlenmeyer flask with sufficient anhydrous perchlorate to make 35–40 cc. of solution. The solvent was then added, and with the flask loosely stoppered, heat was applied, and solvent was evaporated until a saturated solution was obtained at a temperature near the boiling point of the solution. The flask was tightly stoppered and allowed to cool. Except when water or acetone was used as solvent, these solutions did not crystallize upon cooling to 0° or below, but often remained extremely viscous. Extreme cooling and long standing brought about crystallization, when scratching the inner walls of the flask in contact with the solution failed. Attempts to "seed out" these solutions always failed. When crystallization occurred, the amount of solvent necessary to all but dissolve the crystallized portion at 25° was added. A dry tube, about 18–20cc. capacity, was drawn down to prepare for sealing and charged with about a gram of the anhydrous salt. By means of a small glass funnel the tube was partly filled with the saturated solution and the crystallized portion obtained as described above. The solubility tube was then sealed and etched for identification.

The tubes thus prepared contained a solution saturated at a temperature slightly above the bath temperature and in contact both with the anhydrous salt and that crystallized from the solvent. They were rotated end-over-

end in the thermostat usually for 24–48 hours, and then placed in a vertical position to allow the precipitate to settle.

After the solubility tubes had settled clear they were hastily withdrawn from the bath, dried, opened at the constricted upper extremity and samples were drawn off by means of a small pipet into weighed platinum crucibles contained in glass-stoppered weighing bottles. Samples for the solubility data were always taken from each of two or more solubility tubes of duplicate equilibria and the crucibles and containers were all weighed by use of a similar counterpoise. The vapor pressures of the solutions were, as a rule, very low because of extreme solubilities, but even when they were high the glass stoppers fitted so accurately that no loss of solvent occurred.

At the time samples were taken for solubility determination, a sample for density determination was transferred from 1 tube (or portions of 2 tubes) to a 10cc. or 25cc. pycnometer, the stopper of which was a capillary tube very accurately ground. The pycnometer and the pipets used for sampling were stored in glass tubes immersed in the thermostat to attain the bath temperature. In case density determinations were carried out with portions of 2 solubility tubes, only those values were recorded which were obtained through the use of materials, analyses of which duplicated each other.

The platinum crucibles and containers were weighed, a few cubic centimeters of water added, and the crucibles placed upon an electric hot plate until the excess of solvent and water evaporated off. Repeating the treatment with water removed the solvent in all cases completely enough so that the weight of salt could, without danger of explosion, be determined by drying to constant weight at 250° in a current of air dried with phosphorus pentoxide. All solutions were analyzed by this procedure except those made with magnesium perchlorate, in which case, after evaporation of the solvent, enough sulfuric acid was added to convert all the magnesium perchlorate to magnesium sulfate, the solution evaporated to remove excess sulfuric acid and the magnesium sulfate ignited at 650° in an electric furnace. From its weight the perchlorate content of the solutions was calculated. In all cases the anhydrous perchlorates obtained were tested for chloride formed by possible decomposition. Any determination showing such a product was rejected.

Duplicate solubilities as high as 70–75% usually checked within ±0.05%. In cases where low solubility demanded the use of large volumes, glass bulbs of 100 to 125cc. capacity were employed, and weight burets were used for sampling. Weighings were corrected to a vacuum, wherever such corrections were appreciable.

In all cases wherein a manipulation involved exclusion of atmospheric moisture, the operation was carried out in a large, glass-topped desiccator

box, provided with a door for introduction of apparatus and materials, long-sleeved rubber gloves for arm manipulations, and into which a continuous stream of dry air was passed.

Few unusual phenomena were observed during the process of these solubility determinations. High temperature coefficients were observed to accompany high solubilities, and much heat was evolved during solution; in the case of acetone the solution often boiled. The temperature coefficient of the solution of strontium perchlorate in *iso*butyl alcohol is an enormous one, while in *n*-butyl alcohol it is not exceptional. In acetone solutions, no difficulty was encountered in crystallizing the salt from a saturated solution upon cooling.

The most unusual case of extreme solubility was that of anhydrous lithium perchlorate in anhydrous ether. The saturated solution at 25° contains 53.21% of lithium perchlorate and is extremely viscous. The solubility of lithium perchlorate trihydrate in absolute ether is, however, only 0.13%, and in ether saturated with water, 0.09%.

The Solubility Table

The solubilities of the various perchlorates are recorded in the following table. The first 3 horizontal rows contain the actual experimental results, the remaining 4 were obtained by calculation from these.

The last row of figures, comprising the molal solubility per mole of solvent, constitutes the most interesting source of comparison. In general, considering especially the most soluble perchlorates and excluding ether, the molal solubilities in organic solvents are seen to be greater than those in water. The solubility of the perchlorates in the alcohols as a series is shown to decrease with increase in molecular weight of the solvent.

A point of interest is the greater molal solubility in *normal* as compared with *iso*butyl alcohol.

Ethyl acetate and acetone are seen to be equal in solvent action; this is hardly to be expected in view of their very different chemical properties. Acetone solutions crystallize more easily than those in ethyl acetate, show less viscosity and a much greater heat of solution.

All data in the following table refers to 25°.

Summary

1. The preparation of both the anhydrous and crystallized perchlorates of the alkali and alkaline earth metals and ammonium has been described. Some new hydrates were prepared and analyzed.

2. The solubilities at 25° of the anhydrous perchlorates and of lithium perchlorate trihydrate were determined in water, ethyl ether, ethyl acetate, acetone, methyl, ethyl, *n*-propyl and *n*- and *iso*butyl alcohols.

TABLE III

SOLUBILITIES OF PERCHLORATES

SODIUM PERCHLORATE

Solvent	Water	Methyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	*n*-Butyl alcohol	*iso*Butyl alcohol	Acetone	Ethyl acetate	Ethyl ether
Solv. dens.	....	0.78705	0.78515	0.8026	0.8059	0.7981	0.7852	0.8945	0.7081
Soln. dens.	1.6821	1.0561	0.8685	0.8308	0.8167	0.8031	1.0732	0.9574	0.7081
G./100 g. soln.	67.70	33.93	12.82	4.66	1.83	0.78	34.10	8.80	insol.
G./100 cc. soln.	113.88	35.833	11.134	3.871	1.495	0.6264	36.596	8.425	insol.
G./100 g. solv.	209.60	51.355	14.705	4.888	1.864	0.786	51.745	9.649	insol.
G.m.w./100 cc. soln.	0.9299	0.2926	0.0909	0.0316	0.0122	0.00515	0.2988	0.0719	insol.
G.m.w./g.m.w. solv.	0.3084	0.13435	0.0553	0.0240	0.0113	0.0048	0.2453	0.0694	insol.

POTASSIUM PERCHLORATE

Solv. dens.	....	0.78705	0.78515	0.8009	0.8059	0.7981	0.7852	0.8945	0.7081
Soln. dens.	1.0096	0.7878	0.7852	0.8011	0.8060	0.7981	0.7868	0.8945	0.7081
G./100 g. soln.	2.02	0.105	0.012	0.010	0.0045	0.005	0.155	0.0015	insol.
G./100 cc. soln.	2.0394	0.0830	0.0094	0.0080	0.0036	0.0040	0.1179	0.0013	insol.
G./100 g. solv.	2.062	0.1051	0.012	0.010	0.0045	0.0050	0.1552	0.0015	insol.
G.m.w./100 cc. soln.	0.0145	0.00060	0.00070	0.00006	0.00003	0.00004	0.00085	0.00001	insol.
G.m.w./g.m.w. solv.	0.00268	0.00024	0.00004	0.00004	0.00024	0.00003	0.00065	0.00001	insol.

RUBIDIUM PERCHLORATE

Solv. dens.	....	0.78705	0.78515	0.7989	0.8059	0.7981	0.7852	0.8945	0.7081
Soln. dens.	1.0060	0.7875	0.7851	0.7989	0.8059	0.7982	0.7865	0.8945	0.7081
G./100 g. soln.	1.32	0.060	0.009	0.006	0.002	0.004	0.095	0.0016	insol.
G./100 cc. soln.	1.328	0.0472	0.0071	0.0048	0.0016	0.0032	0.0745	0.0014	insol.
G./100 g. solv.	1.338	0.060	0.009	0.006	0.002	0.004	0.095	0.016	insol.
G.m.w./100 cc. soln.	0.00718	0.00025	0.00004	0.00003	0.00001	0.00002	0.00040	0.00001	insol.
G.m.w./g.m.w. solv.	0.00130	0.00011	0.00002	0.00002	0.00001	0.00002	0.00030	0.00006	insol.

TABLE III (*Continued*)

Solvent	Water	Methyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	*n*-Butyl alcohol	*iso*Butyl alcohol	Acetone	Ethyl acetate	Ethyl ether
CESIUM PERCHLORATE									
Solv. dens.	....	0.78735	0.78517	0.7993	0.8059	0.7981	0.7852	0.8945	0.7081
Soln. dens.	1.0165	0.7878	0.7852	0.7993	0.8059	0.7981	0.7859	0.8945	0.7081
G./100 g. soln.	1.93	0.093	0.011	0.006	0.006	0.007	0.150	insol.	insol.
G./100 cc. soln.	1.961	0.0734	0.0086	0.0045	0.0048	0.0056	0.1178	insol.	insol.
G./100 g. solv.	2.000	0.093	0.011	0.006	0.006	0.007	0.150	insol.	insol.
G.m.w./100 cc. soln.	0.00844	0.00032	0.00004	0.00002	0.00002	0.00002	0.00051	insol.	insol.
G.m.w./g.m.w. solv.	0.00155	0.00013	0.00002	0.00002	0.00002	0.00002	0.00057	insol.	insol.
AMMONIUM PERCHLORATE									
Solv. dens.	....	0.78735	0.78515	0.7993	0.8059	0.7981	0.7852	0.8945	0.7081
Soln. dens.	1.0982	0.8218	0.79505	0.8016	0.8069	0.7988	0.7997	0.8947	0.7081
G./100 g. soln.	19.95	6.41	1.872	0.385	0.017	0.127	2.21	0.032	insol.
G./100 cc. soln.	21.91	5.268	1.488	0.3086	0.0137	0.1154	1.768	0.0286	insol.
G./100 g. solv.	24.922	6.862	1.907	0.3865	0.0170	0.1272	2.260	0.032	insol.
G.m.w./100 cc. soln.	0.18647	0.04483	0.01266	0.00263	0.00012	0.00098	0.01504	0.00024	insol.
G.m.w./g.m.w. solv.	0.03821	0.01871	0.00747	0.00198	0.00011	0.00080	0.01117	0.00024	insol.
BARIUM PERCHLORATE									
Solv. dens.	....	0.78705	0.78517	0.7989	0.8059	0.7981	0.7852	0.8923	0.7081
Soln. dens.	1.9403	1.7507	1.4157	1.2145	1.1342	1.1171	1.4607	1.5236	0.7081
G./100 g. soln.	66.48	68.46	55.48	43.07	36.78	35.99	55.49	53.04	insol.
G./100 cc. soln.	128.99	119.85	78.543	52.309	41.716	36.667	81.054	80.812	insol.
G./100 g. solv.	198.33	217.06	124.62	75.654	58.168	56.226	124.67	112.95	insol.
G.m.w./100 cc. soln.	0.3836	0.3564	0.2336	0.15555	0.12405	0.1090	0.2410	0.2403	insol.
G.m.w./g.m.w. solv.	0.10625	0.2068	0.1707	0.1352	0.1282	0.1239	0.21525	0.29585	insol.

TABLE III (*Continued*)

CALCIUM PERCHLORATE

Solvent	Water	*Methyl* alcohol	Ethyl alcohol	*n*-Propyl alcohol	*n*-Butyl alcohol	*iso*Butyl alcohol	Acetone	Ethyl acetate	Ethyl ether
Solv. dens.....	....	0.78705	0.78517	0.7989	0.8059	0.7981	0.7852	0.8945	0.7081
Soln. dens.....	1.7191	1.6155	1.4342	1.3806	1.2868	1.0903	1.1475	1.3325	0.7098
G./100 g. soln.....	65.35	70.36	62.44	59.17	53.17	36.29	38.18	43.06	0.26
G./100 cc. soln.....	112.34	113.68	89.551	81.690	68.419	39.567	43.812	57.377	0.1846
G./100 g. solv.....	188.60	237.38	166.24	144.92	113.54	56.961	61.860	75.623	0.2607
G.m.w./100 cc. soln.....	0.4701	0.4758	0.3747	0.3418	0.2863	0.1656	0.1833	0.2401	0.0008
G.m.w./g.m.w. solv.....	0.1422	0.3182	0.3204	0.3643	0.3520	0.1766	0.1503	0.2787	0.0008

STRONTIUM PERCHLORATE

Solv. dens.....	....	0.78705	0.78517	0.7989	0.8059	0.7981	0.7852	0.89457	0.7081
Soln. dens.....	2.0837	1.6771	1.5539	1.4266	1.3394	1.2022	1.4984	1.4717	0.7081
G./100 g. soln.....	75.59	67.95	64.37	58.40	53.16	43.78	60.01	52.10	insol.
G./100 cc. soln.....	157.51	113.95	100.01	83.31	71.205	52.63	89.92	76.67	insol.
G./100 g. solv.....	309.67	212.01	180.66	140.38	113.49	77.87	150.06	136.93	insol.
G.m.w./100 cc. soln.....	0.5497	0.3977	0.3491	0.2988	0.2485	0.1837	0.3138	0.2676	insol.
G.m.w./g.m.w. solv.....	0.1947	0.2371	0.2904	0.2943	0.2935	0.1633	0.4040	0.3827	insol.

MAGNESIUM PERCHLORATE

Solv. dens.....	....	0.78705	0.78515	0.7989	0.8059	0.7981	0.7864	0.89457	0.7081
Soln. dens.....	1.4720	1.1057	0.9518	1.1926	1.1399	1.0609	1.0798	1.3057	0.7101
G./100 g. soln.....	49.90	34.14	19.33	42.33	39.16	31.27	30.015	41.49	0.29
G./100 cc. soln.....	73.453	37.749	18.398	50.483	44.638	33.174	32.410	54.173	0.2059
G./100 g. solv.....	99.601	51.838	23.962	73.400	64.366	45.497	42.888	70.911	0.2908
G.m.w./100 cc. soln.....	0.3294	0.1691	0.8241	0.2261	0.2000	0.1486	0.1452	0.2427	0.0009
G.m.w./g.m.w. solv.....	0.0804	0.0744	0.0494	0.1975	0.21365	0.1510	0.11155	0.2798	0.0010

TABLE III (*Concluded*)

ANHYDROUS LITHIUM PERCHLORATE

Solvent	Water	Methyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	*n*-Butyl alcohol	*iso*Butyl alcohol	Acetone	Ethyl acetate	Ethyl ether
Solv. dens.	....	0.78705	0.78517	0.7989	0.8059	0.7981	0.7852	0.89457	0.70817
Soln. dens.	1.2683	1.3849	1.3173	1.2006	1.1326	1.0602	1.3233	1.3005	1.2116
G./100 g. soln.	37.385	64.57	60.28	51.22	44.23	36.73	57.72	48.75	53.21
G./100 cc. soln.	47.42	89.44	79.41	61.49	49.25	38.94	76.38	63.40	64.47
G./100 g. solv.	59.71	182.25	151.76	105.00	79.31	58.05	136.52	95.12	113.72
G.m.w./100 cc. soln.	0.4457	0.8406	0.7463	0.5779	0.6646	0.3660	0.71785	0.5958	0.6059
G.m.w./g.m.w. solv.	0.1011	0.5487	0.6569	0.5929	0.5536	0.4043	0.7450	0.7875	0.7920

LITHIUM PERCHLORATE TRIHYDRATE

Solv. dens.	....	0.78705	0.78517	0.7989	0.8059	0.7981	0.7852	0.89457	0.70817
Soln. dens.	....	1.1420	1.0241	0.9349	0.9082	0.8887	1.0965	1.0402	0.7091
G./100 g. soln.	....	60.95	42.16	26.82	21.40	18.85	49.04	26.35	0.196
G./100 cc. soln.	....	69.61	43.18	25.07	19.435	16.75	53.77	27.41	0.139
G./100 g. solv.	....	156.08	72.90	36.63	27.22	23.23	96.23	35.78	0.196
G.m.w./100 cc. soln.	....	0.4338	0.2691	0.1563	0.1211	0.1044	0.3351	0.17085	0.00086
G.m.w./g.m.w. solv.	....	0.31165	0.20925	0.1372	0.1257	0.1073	0.3482	0.1964	0.0905

3. The purification of the solvents was described.

4. The experimental methods were described and unusual features in the results were discussed.

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ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CONSTITUTION OF FERRIC OXIDE HYDROSOL FROM MEASUREMENTS OF THE CHLORINE- AND HYDROGEN-ION ACTIVITIES

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In the course of a study of the heat of coagulation of ferric oxide hydrosol with electrolytes[2] it was found impossible to give a quantitative interpretation of the results with sols of low purity because of lack of knowledge of the nature and distribution of the electrolytes in these sols. This investigation was carried out with the purpose of supplying these data through a study of the chloride- and hydrogen-ion activities of the sols[3] and of solutions of ferric chloride.

The sol is regarded as an aqueous solution of ferric chloride and hydrochloric acid in hydrolytic equilibrium in which are dispersed particles of hydrous ferric oxide which adsorb varying amounts of ferric chloride, hydrogen chloride, ferric and hydrogen ions. The activity coefficient for chloride ion was first determined in ferric chloride solutions of various concentrations in which hydrolysis was minimized by keeping the solution acid with nitric or sulfuric acid. From similar measurements on ferric chloride solutions which contained no added acid and had been allowed to come to hydrolytic equilibrium it was possible to deduce the amount of ferric chloride and of hydrochloric acid in these solutions. Assuming then that the dispersion medium of a ferric oxide sol[4] has the same constitution as a ferric chloride solution of the same content of chloride ion, it was possible to arrive at the constitution of the hydrosols from measurements of their chloride-ion activities.

Further light on the constitution of the sols was obtained by means of measurements of the hydrogen-ion activities. For this purpose a special

[1] National Research Fellow in Chemistry.

[2] Browne and Mathews, THIS JOURNAL, **43**, 2336 (1921).

[3] Pauli and Matula, *Kolloid-Z.*, **21**, 49 (1917), made such measurements with one sol of high purity and lower concentration.

[4] HCl and $FeCl_3$ were the only electrolytes in the sols.