corresponding solubilities were calculated by dividing the values of the specific conductance so obtained by the appropriate values of the equivalent conductance, which last were derived in the case of the first two salts from the values for the separate ions at zero concentration, and in the case of the calcium sulphate from measurements (also presented above) of the conductance of solutions of it of known concentration. The final solubility values will be found in Tables V and XI, on pages 55 and 63. The heats of solution of silver chloride and barium sulphate were also calculated from these data.

In the case of calcium sulphate, the investigation included the study of the solubility relations of the three forms: gypsum, soluble anhydrite, and ordinary anhydrite. These relations are represented graphically in Fig. 2 on page 65. The transition temperature for the metastable system gypsum, soluble anhydrite, solution, was found, from the point of intersection of the solubility curves, to be about 97°. The solubility of the ordinary anhydrite was shown to decrease enormously with rising temperature, namely from 29.0 milli-equivalents per liter at 60°, where, according to van't Hoff, it is in stable equilibrium with gypsum, to 0.7 milli-equivalents per liter at 218°.

The ion concentrations in the saturated solutions of calcium sulphate have also been calculated and presented in Table XIII, on page 64.

The ionization relations of calcium sulphate have been compared with those for magnesium sulphate previously investigated in this laboratory by Noyes and Melcher. At 18° the degrees of ionization of the two salts are nearly identical; but at 100 and 156° the ionization of the calcium salt is a few per cent. less than that of the magnesium salt at corresponding concentrations.

This investigation has been carried out under the direction of Professor A. A. Noyes with the aid of a grant made to him by the Carnegie Institution of Washington. It is desired to express here grateful acknowledgment of this financial aid, by which this research has been made possible.

BOSTON, October. 1909.

THE PREPARATION OF PERCHLORIC ACID FROM SODIUM PERCHLORATE.[1]

BY FRANK C. MATHERS.

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Most of the methods for the preparation of perchloric acid depend upon the distillation under reduced pressure of a mixture of a perchlorate

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[1] NOTE.—This investigation was the result of a search for a cheap and convenient method for the preparation of perchloric acid, to be used in making perchlorate baths for the electroplating and refining of metals as described in the United States Patent, No. 931,944, issued to the author.

and sulphuric acid or of a crude perchloric acid that has been prepared by the decomposition of aqueous chloric acid by heat, by the action of sulphuric acid upon barium perchlorate, or by the action of hydrofluosilicic acid upon potassium perchlorate.

Kreider[1] has described a method which avoids this troublesome distillation under reduced pressure, which is easy of manipulation and which gives a very pure perchloric acid. His method is based upon the reaction expressed by this equation:

$$NaClO_4 + \text{conc. } HCl\ (+ \text{ excess conc. } HCl) = NaCl + HClO_4.$$

Solid dry sodium perchlorate is treated with an excess of concentrated hydrochloric acid. The mixture is then filtered and the residue of sodium chloride which is almost insoluble in the excess of hydrochloric acid is washed with concentrated hydrochloric acid. The filtrate is a mixture of perchloric acid, hydrochloric acid and small amounts of the sodium salts of these acids due to the slight solubility of the sodium chloride in the hydrochloric acid solution. By heating this filtrate until white fumes of perchloric acid are evolved, the hydrochloric acid is volatilized and the perchloric acid remains behind. The boiling points of the hydrochloric acid and the perchloric acid with 2 molecules of water (119 and 203° respectively) are so far apart that a very satisfactory separation is obtained.

The object of this research was to determine the best conditions and the proper quantities of reagents to use in order to obtain the best results from this process of Kreider, since the original article only gave a qualitative description of the method.

Twenty grams of sodium perchlorate (weighed to 1 mg.) was placed in a 100 cc. beaker and treated with the concentrated hydrochloric acid. The contents of the beaker were filtered upon a Gooch crucible and the residue of sodium chloride washed with ten 1 cc. portions of concentrated hydrochloric acid. The filtrate, which contained the aqueous perchloric acid and the excess of hydrochloric acid together with small amounts of the sodium salts of these acids, was evaporated upon a hot plate to volatilize the hydrochloric acid. The residue which did not volatilize below a temperature of 150° consisted of aqueous perchloric acid whose purity and yield depended upon the conditions of the experiment. These samples of perchloric acid were analyzed to determine the free perchloric acid, the sodium perchlorate and the hydrochloric acid. The residues of sodium chloride that were obtained by the first filtration upon the Gooch crucibles, were analyzed to determine the sodium perchlorate.

Methods of Analysis.—Free acids were determined by titration using

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[1] Kreider, *Am. J. Sci.* [3], 49, 443; *Z. anorg. Chem.*, 9, 343. Treadwell and Hall, "Quantitative Chemistry," Vol. 2, page 47 (1904).

methyl orange as indicator. The end point with perchloric acid was decisive and satisfactory. Volhard's method was used for the volumetric determination of the chlorides. The perchlorates in the free perchloric acid were determined by evaporating a measured portion to dryness in a platinum dish. The dish was then heated to near redness until the perchlorates were decomposed to chlorides. The end of this decomposition was easily detected since the perchlorates were easily fusible and the chlorides were infusible at this temperature. The total residue which consisted essentially of sodium chloride was calculated to sodium perchlorate. Of course this method would only correct results with samples containing perchloric acid, sodium perchlorate and easily volatile substances such as hydrochloric acid. The estimation of perchlorates in the presence of chlorides depends upon the determination of the difference between the chlorine in a sample that has been treated to decompose the perchlorates into chlorides and in an untreated sample. This decomposition can be accomplished very easily by the method of Dittrich and Hollenback.[1] The perchlorate is fused for several hours with sodium nitrite. After cooling, the fused mass is dissolved in water and the chlorine is determined by the method of Volhard. Porcelain dishes are attacked by the fused sodium nitrite so platinum vessels must be used. The sodium nitrite that was used in this research contained chlorine so a blank was determined and the proper correction was applied to each analysis. This method gave uniformly accurate results and was satisfactory in every way.

Materials Used.—A commercial preparation of sodium perchlorate was used. Its composition was: NaCl, 1.76, 1.86; $NaClO_4$, 95.38, 95.77 per cent.; $NaClO_3$, trace.

Commercial barium perchlorate was used. The material was "caked" in the bottle and an average sample for analysis was difficult to obtain. An analysis showed 53.5 per cent. of ClO_4. The C. P. hydrochloric acid which was used showed a specific gravity (spindle) of 1.16 at 24°. The commercial acid which was used in one experiment had a specific gravity of 1.14 at 24°, and each cc. contained 0.00097 gram of non-volatile matter.

TABLE I.—EFFECT OF WATER.

The sodium perchlorate (20 grams) was dissolved in 7 cc. of water at 105° and then 20 cc. concentrated hydrochloric acid was added. For comparison the results without water are included in this table.

Grams water added.	$HClO_4$ in the filtrate in terms of $NaClO_4$.		$NaClO_4$ in filtrate.	Total ClO_4 in filtrate. In terms of $NaClO_4$.		$NaClO_4$ in NaCl residue.
cc.	Grams.	Per cent.	Grams.	Grams.	Per cent.	Gram.
7.0	15.48	81.6	2.63	18.11	94.7	0.2
0.0	16.97	88.4	1.65	18.62	97.4	0.46

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[1] Dittrich and Hollenback, *Ber.*, **38**, 751 (1905).

This data shows that water should not be added.

TABLE II.—EFFECT OF THE QUANTITY OF HYDROCHLORIC ACID.

Cc. of HCl.	$HClO_4$ in the filtrate. In terms of $NaClO_4$. Grams.	Per cent.	$NaClO_4$ in filtrate. Grams.	Total ClO_4 in filtrate. In terms of $NaClO_4$. Grams.	Per cent.	$NaClO_4$ in NaCl residue. Grams.
10	13.65	71.4	1.91	15.56	81.4	2.72
15	15.4	80.5	1.61	17.05	89.2	1.46
20	16.97	88.4	1.65	18.62	97.4	0.46
25	18.13	94.8	0.84	18.97	99.2	0.2
30	18.35	96.0	0.79	19.14	100.1	0.18
50	18.65	97.6	0.63	19.28	100.8	0.34

This table shows that 25 to 30 cc. of hydrochloric acid should be used for each 20 grams of sodium perchlorate.

TABLE III.—TO FIND THE TEMPERATURE NEEDED TO EXPEL THE HYDROCHLORIC ACID FROM THE FILTRATE.

Temperature.	Cl in the filtrate. In terms of $NaClO_4$. Grams.
120°	2.006
130°	0.06
135°	0.0
145°	White fumes of $HClO_4$.

The filtrates containing the perchloric and hydrochloric acids were heated upon a hot plate. The sides of the beaker should be brought to the temperature of the experiment since, otherwise, the drops of the liquid which condense upon the upper part of the beaker retain hydrochloric acid. When the temperature of the entire beaker was brought to 135° there was not enough hydrochloric acid remaining to give an opalescence with silver nitrate. All of the hydrochloric acid could probably have been removed by maintaining the temperature somewhat below 135° for a period of time but this experiment was not tried. This table shows that all of the hydrochloric acid is volatilized at a temperature of 135°.

TABLE IV.—LOSS OF PERCHLORIC ACID DURING THE VOLATILIZATION OF THE HYDROCHLORIC ACID.

Volume of aqueous $HClO_4$ used.	Cc. of substances added. H_2O.	HCl (conc.).	Grams of $HClO_4$ present.	$HClO_4$ lost. Gram.	Per cent.
40	0	..	6.97	0.09	0.13
40	50	..	6.97	0.14	0.20
40	..	90	6.97	0.19	0.27

The solutions were heated upon the hot plate until the temperature reached 135°. Any loss as small as that shown in this table can be neglected in a method of preparation.

TABLE V.—AMOUNT OF WASHING NEEDED TO REMOVE THE PERCHLORIC ACID FROM THE SODIUM CHLORIDE RESIDUES.

The residue was first drained by suction. It was then washed with 5 1 cc.-portions of concentrated hydrochloric acid, again drained by suction, then washed with a second five 1 cc.-portions of acid, etc. Each five 1 cc.-portions were saved separately and analyzed.

Conc. HCl used in washing.	$HClO_4$ washed from the residue of NaCl. Grams.
First 5 1 cc.-portions	large amounts.
Second 5 1 cc.-portions	1.65
Third 5 1 cc.-portions	0.19
Fourth 5 1 cc.-portions	0.08

After washing with twenty portions of acid, 0.06 gram of sodium perchlorate still remained in the residue. This table shows that ten 1 cc.-portions of concentrated hydrochloric acid is the most economical amount to use in washing the residue from 20 grams of sodium perchlorate and 25 cc. of concentrated hydrochloric acid.

In one experiment 20 grams of barium perchlorate were treated with 60 cc. of hydrochloric acid. The precipitate of barium chloride was very bulky and voluminous, entirely filling an ordinary Gooch crucible. The 60 cc. of hydrochloric acid just made the residue liquid enough so that it could be poured upon the filter. The yield of perchloric acid was 80.9 per cent. of theory. Washing with ten 1 cc.-portions of hydrochloric acid failed to wash the perchloric acid out of such a bulky residue. Another experiment showed that "commercial" hydrochloric acid did not give as good results as the "C. P." acid. This was no doubt due to the lower concentration of the "commercial" acid. The yield of perchloric acid was 88.7 per cent. as compared to 96.0 per cent. for the "C. P." acid. Potassium perchlorate cannot be used.

Summary.

These experiments were made to determine the best conditions for the preparation of perchloric acid by the action of concentrated hydrochloric acid upon sodium perchlorate.

The sodium chloride is insoluble in the excess of concentrated hydrochloric acid and can be separated from the perchloric and hydrochloric acids by filtering upon an asbestos filter and by washing with concentrated hydrochloric acid. By heating the filtrate, the hydrochloric acid can be volatilized away from the perchloric acid. The best conditions are: Use 25 to 30 cc. of concentrated hydrochloric acid for each 20 grams of sodium perchlorate. Do not add any water to the substances. Filter out the sodium chloride residue and wash with ten 1 cc. portions of concentrated hydrochloric acid. Heat the filtrate and washings to 135° to volatilize the hydrochloric acid. The yield of perchloric acid is about 95 per cent. of the theoretical. Only about 1 per cent. of the sodium

perchlorate is lost in the sodium chloride residues. The other 4 per cent. is in the perchloric acid as sodium perchlorate. The perchloric acid is free from chlorides. The process does not work with potassium perchlorate and is unsatisfactory with barium perchlorate.

UNIVERSITY OF INDIANA, BLOOMINGTON.

ORGANIZATION OF INDUSTRIAL RESEARCH.[1]

BY WILLIS R. WHITNEY.

Received November 6, 1909.

The intimate connection between the purely scientific research of a people and its advance in the art of good living cannot be too frequently discussed. The organization of industrial research involves arranging and maintaining a body of involute parts as an operative whole of highest efficiency. It is never perfectly accomplished, and the fact that improvement can always be made is an incentive for its discussion.

A recent copy of *Life* has this to say, which, without straining, bears directly upon industrial research:

"This is the most interesting country in the world. The game here is the biggest that is being anywhere played. The problems of humanity that are being worked out here are the greatest problems under consideration, and the prospect of solving them is better than it is anywhere else."

Lord Bacon said: "The real and legitimate goal of the sciences is the endowment of human life with new invention and riches." He, in turn, cited King Solomon, who said, "it is the glory of God to conceal a thing, but the glory of a king to search it out."

Bacon distinguishes three degrees of ambition:

First, that of men anxious to enlarge *their own* power *in* their own country. This is "vulgar and degenerate."

Second, that of men who strive to enlarge the power and empire of their *country* over mankind. This is "more dignified, but not less covetous."

Third, that of those who strive to enlarge the power and empire of *mankind* in general over the *universe*. Evidently this is the best, and is the real ambition, whether recognized or not by himself, of any good experimenter.

For purposes of systematic analysis, the subject, "Organization of Industrial Research," may be divided into two parts:

Part one, the personal or mental organization, with its requirements, etc.

Part two, the objective or material organization.

For brevity, these may be called the mind and the matter organizations.

The former, or personal, I will subdivide into such parts as:

Its training and characteristics.

Division of its labors.

Its records, etc.

The objective or matter organization, I divide into:

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[1] An address delivered at the Twentieth Anniversary of Clark University, Sept. 17, 1909.