Summary

1. Grignard reagents in ether solution are chemiluminescent on oxidation by oxygen only if the magnesium is attached directly to an unsaturated carbon atom. This rule is shown to hold for both aliphatic and aromatic compounds, in all cases investigated.

2. The nature of the solvent affects the intensity of the luminescence, but apparently not the wave length.

3. No chemiluminescence is found when zinc or mercury is used instead of magnesium.

4. The wave length and intensity of the radiation are affected by the nature of the reacting halogen.

5. The wave length and the intensity are affected by the nature of the organic radical involved, and especially by the nature of substituted groups in the cyclic compounds. The effect depends on (a) the position of the substituent group; (b) the chemical nature of the substituent group. It is shown that the mass of the substituent is not the controlling factor.

6. Certain cases of very bright chemiluminescence are described; the luminescence of *p*-chlorophenylmagnesium bromide is believed to be the brightest yet recorded.

7. A method (apparently new) of preparing chlorine-containing Grignard compounds is described.

8. Many Grignard compounds give light when treated with chloropicrin and with bromopicrin. This light is not the same as that given out on oxidation with oxygen.

9. Many Grignard compounds and especially their oxidation-products are found to be fluorescent in ultraviolet light.

10. Two tables are given listing the luminescent properties of more than 60 compounds, of which over 40 are luminescent.

Columbia, Missouri

[Contribution from the Chemical Laboratory of the University of Illinois]

THE SEPARATION AND DETERMINATION OF POTASSIUM AND SODIUM. A PERCHLORATE PRECIPITATION PROCESS USING NORMAL BUTYL ALCOHOL

By G. Frederick Smith

Received June 14, 1923

The perchlorate method for the separation and determination of potassium and sodium has been quite generally accepted as a satisfactory substitute for the chloroplatinate procedure. The use of absolute ethyl alcohol in the perchlorate procedure is a pronounced disadvantage. The method has the further disadvantage of being an extraction process. This method of extracting a mixture of salts with a solvent for one of them is necessarily inefficient, since the crystals of one may be more or less surrounded by a coating of the other salt. It would obviously be a considerable improvement if the use of ethyl alcohol and the inefficient extraction type of procedure could be entirely eliminated. The present paper shows how both of these improvements can be accomplished and also simplifies the procedure with consequent increase in accuracy.

Studies in the improvement of the perchlorate separation of potassium and sodium are desirable, as indicated by recent work in the field by several careful observers including those of Baxter and Kobayashi,[1] Baxter and Rupert[2] and Gooch and Blake.[3] The most complete work on the perchlorate method is that of Morris[4] which contains an extensive bibliography. Few further references to the literature of the subject are therefore necessary here.

The Method

The process, in brief, consists in the precipitation of potassium perchlorate from solution in warm water, in the presence of sodium perchlorate, by the slow addition of a proportionally large volume of *N*-butyl alcohol containing 0.5–1% of perchloric acid dihydrate. The solution together with the precipitated potassium perchlorate is then boiled for 30 seconds, cooled to room temperature and filtered using a Monroe or Gooch crucible. The precipitate is washed with butyl alcohol, dried at 150–250° for 1/2 to 1 hour and weighed as potassium perchlorate. The sodium is determined in the filtrate by evaporation of the solvent and conversion of the sodium perchlorate to sulfate, and is weighed as such in the usual manner. The method is best suited to the determination of sodium by difference, after weighing the mixed potassium and sodium chlorides.

Preparation of Materials

***Normal* Butyl Alcohol.**—This material is readily obtainable on the market at the present time at a moderate price. The alcohol used in this research had a boiling range of 112–118°; d_4^{25} 0.8065. It was distilled as received without further treatment, and the first and last 5% discarded.

Perchloric Acid.—The acid used was prepared by the method of Willard.[5] This material was converted to the true dihydrate,[6] $HClO_4 \cdot 2H_2O$ by a method to be described in a subsequent paper. The dihydrate was used to acidify the butyl alcohol employed in this investigation as well as for converting weighed portions of potassium and sodium chlorides to perchlorates.

Sodium and Potassium Perchlorates.—These materials were prepared

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[1] Baxter and Kobayashi, This Journal, **39**, 249 (1917); **42**, 735 (1920).

[2] Baxter and Rupert, *ibid.*, **42**, 2048 (1920).

[3] Gooch and Blake, *Am. J. Sci.*, **44**, 381 (1917).

[4] Morris, *Analyst*, **45**, 349 (1920).

[5] Willard, This Journal, **34**, 1480 (1912).

[6] 70% perchloric acid may be used wherever this material is mentioned in this paper.

from sodium and potassium chlorides that had been twice recrystallized from aqueous solution using hydrogen chloride. The chlorides thus obtained were converted to perchlorates with an excess of pure perchloric acid followed by crystallization of the perchlorates and filtration with centrifugal drainage. The perchlorates thus obtained were dried at 250° and were found to be free from chlorides.

Sodium and Potassium Chlorides.—These were a foreign firm's best product dried at 250° before use.

Solubility Determinations

The solubilities of sodium perchlorate in *n*-butyl alcohol both at ordinary temperature and at the boiling point of the resulting solutions, in the absence and in the presence of increasing percentages of perchloric acid, are important in connection with the present investigation. Solubility tubes were prepared containing an excess of anhydrous sodium perchlorate together with the pure butyl alcohol or alcohol containing 0.25%, 0.5% or 1.5% of perchloric acid dihydrate by weight. The sealed glass tubes were revolved endwise during 5–6 hours at room temperature of 25° with variation of less than 3°. The temperature coefficient for the solubilities involved was known to be high, but since all experiments were conducted simultaneously and comparative results only were desired, accurate temperature control was not necessary. The saturated solutions thus obtained were allowed to settle, samples were withdrawn from the clear supernatant liquid and the sodium perchlorate was determined as described by Willard and Smith.[7] The solubility determinations of the same solutions at the boiling point were carried out in a specially prepared all-glass refluxing apparatus. The solutions in presence of excess of solute were gently boiled for $^1/_2$ to 1 hour and samples were withdrawn from the continuously boiling solution with a special pipet provided with a filtering medium in its lower stem and maintained hot by being inserted through the reflux condenser into the hot vapors over the solution.

The results obtained are reported by graph (Fig. 1) rather than by table to avoid a wrong conclusion concerning their accuracy. The determinations were carried out in duplicate to exclude the possibility of gross error.

By study of the values reported in Fig. 1 it is seen that the solubility of anhydrous sodium perchlorate at 25° in the butyl alcohol employed is approximately 3%. The addition of 0.25%, 0.5% and 1% perchloric acid dihydrate is progressively without appreciable effect, the solubility still remaining approximately 3% in the presence of 1% of acid. The solubility of sodium perchlorate in the pure alcohol at the boiling point of the solution is approximately 7.6% while with addition of perchloric acid dihydrate the solubility increases uniformly until at 1% acid concentration the solu-

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[7] Willard and Smith, This Journal, 45, 291 (1923).

bility of the sodium salt has reached approximately 9%. In addition to the values included in Table I it was found that the butyl alcohol when treated with 1% of water by volume and 1% of perchloric acid dihydrate by weight, dissolved at 25° approximately 4.5% of sodium perchlorate, and this value was increased to approximately 5% for butyl alcohol containing 1% of acid and 3% of water for the same temperature. It has been shown by Willard and Smith[7] and by Gomberg[8] that equilibrium for solutions of perchlorates in organic solvents is slowly attained and that there is a pronounced tendency towards supersaturation. This observation was found to hold for the solution of sodium perchlorate in butyl alcohol, so that in actual practice solubilities in excess of those given are often obtained. Determinations of solubilities of sodium perchlorate in butyl alcohol containing 1% of perchloric acid dihydrate with 1% and 3% of water at the boiling point were not made but the values are known to be much higher than for the same solutions without water and at the boiling temperature.

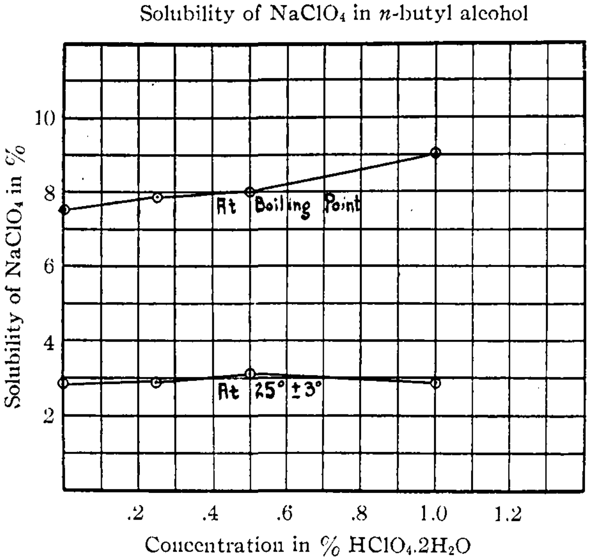

Fig. 1

The solubilities of potassium perchlorate in the same solvent were made omitting determinations for boiling solutions. In these determinations 100 cc. or more of solvent was employed, the solutions resulting from the equilibria attained after 5–20 hours' agitation were filtered through a Monroe crucible and the potassium perchlorate in the weighed filtrates was recovered and converted to potassium sulfate, from the weight of which the potassium perchlorate originally dissolved was de-

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[8] Gomberg, This Journal, **45**, 403 (1923).

termined. The determinations were carried out in duplicate and the results of these closely agreeing duplicates are reported in Table I.

TABLE I

THE SOLUBILITY OF POTASSIUM PERCHLORATE IN n-BUTYL ALCOHOL WITH AND WITHOUT VARIOUS ADDITIONS OF WATER AND PERCHLORIC ACID

Perchloric acid added as $HClO_4.2H_2O$ in parts by weight. Water was added in parts by volume. Temperature, 25° ± 3°.

Additions to butyl alcohol		Amount of solution analyzed	K_2SO_4 found	$KClO_4$ dissolved[a]
Acid % +	Water %	Cc.	G.	Mg./100 cc.
None	None	125	0.0010	1.35
0.25	...	110	.0007	1.0
0.5	...	102	.0007	1.0
1.0	...	115.	.0006	1.9
..	1.0	96	.0012	2.0
1.0	1.0	98	.0008	1.4
..	3.0	100	.0023	3.8
1.0	3.0	95	.0010	1.6
0.5	3.0	84	.0006	1.2
1.0	5.0	97	.0014	2.3

[a] One-third of these values represents the amount calculated as K_2O.

It will be seen from Table I that for butyl alcohol, as demonstrated for ethyl alcohol by Thin and Cumming[9] and by Baxter and Kobayashi,[1] the solubility of potassium perchlorate is materially diminished by the addition of perchloric acid. This effect is very pronounced for butyl alcohol containing up to 5% of water. The data of Table I led to the choice of butyl alcohol containing 1% of perchloric acid dihydrate and 3% of water as the best solvent to be used in the separation and determination of potassium and sodium in the manner to be described.

The Precipitation of Potassium Perchlorate and Separation from Sodium Perchlorate

The mixed chlorides of potassium and sodium (free from sulfate) obtained by the J. Lawrence Smith or other method are evaporated to dryness with an excess of perchloric acid. A second evaporation is desirable when the amount is great. Two or three cc. of water is then added according to whether the amount of potassium is low or high, respectively, and the mixed perchlorates are then dissolved by gently swirling the covered beaker over a free flame. The sodium perchlorate is extremely soluble. Potassium perchlorate dissolves to the extent of 20 mg. per cc. at 25° as shown by Willard and Smith[7] and more than 200 mg. at 99° as shown by Calzolari.[10] Sixty-five or 100 cc. of 0.5–1.0% perchloric acid butyl alcohol solution, according to whether 2 cc. or 3 cc. of water has been added to dissolve the mixed perchlorates, is heated to boiling (using a wire gauze

[9] Thin and Cumming, *J. Chem. Soc.*, **107**, 361 (1915).

[10] Calzolari, *Acc. Sci. Med. Ferrara*, **85**, 150 (1911).

and free flame) and added to the warm, aqueous, perchlorate solution slowly with vigorous stirring. The potassium perchlorate is slowly precipitated as the addition of alcohol continues and after all has been added the solution is boiled gently in the covered beaker for half a minute and cooled to room temperature.

The resulting solution and precipitate are filtered through a weighed Monroe or Gooch crucible, the potassium perchlorate is transferred and the beaker walls are rinsed with the butyl alcohol solution used as precipitant (for precautions involved in the preparation of Gooch crucible asbestos for acid butyl alcohol solutions and other manipulative details, see Willard and Smith).[11] The precipitate in the crucible is washed with 8 to 10 portions of 1 to 2 cc. each of precipitant, thus limiting the filtrate and washings to 125–150 cc. It is dried at 150–250°, cooled and weighed. From the weight of the perchlorate obtained, the potassium chloride or oxide present is calculated.

The filtrate and washings from the determination of potassium are diluted with considerable water, forming 2 layers, and the whole is evaporated on the steam bath in such a way as to avoid any condensation on the upper part of the beaker, thus hastening the evaporation. It is well to add 5 to 10 cc. of water at the end of the evaporation to make the removal of organic matter more complete as the solution becomes concentrated. By such treatment a colorless residue of sodium perchlorate and perchloric acid can be obtained. When any brown color remains after this treatment, remove the watch glass supports and heat the beaker gradually on the hot plate until fumes of perchloric acid are evolved. Allow the perchloric acid to continue just at the fuming point until the organic matter is oxidized. Add a few drops of perchloric acid if not enough is present. When the brown color is removed 0.5 cc. of concd. sulfuric acid is added, the watch glass supports are replaced and the acid is fumed off using a wire gauze and free flame. The beaker is cooled, 5–10 cc. of water added and the cover glass and beaker walls are washed. The sodium sulfate solution is then transferred to a platinum crucible, previously weighed with cover, the solution evaporated and the sodium sulfate ignited as usual.

The separation of potassium and sodium perchlorates by the process given was tested by the analysis of 10 mixtures of potassium chloride and sodium chloride and the results are reported in Table II.

Table II shows that small or large amounts of potassium can be separated from large or small amounts, respectively, of sodium by one precipitation, results being obtained which agree excellently with the calculated values. An exceptional compensation of errors accounts for this fact. The amount of potassium perchlorate dissolved which would make results low is counterbalanced by the occlusion of sodium perchlorate.

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[11] Willard and Smith, THIS JOURNAL, 44, 2823 (1922).

In all cases except those in which a very small amount of sodium is present no solubility correction for potassium is necessary. Direct determination of sodium in the filtrate from potassium gives results somewhat high in accordance with the higher molecular weight of potassium sulfate than that of sodium sulfate. The average plus and minus errors for the 10 analyses of Table II show the potassium chloride found to be 0.2 mg. low for an average sample of 0.1441 g. of KCl and the sodium chloride found 0.6 mg. high for an average sample of 0.1603 g. of NaCl.

TABLE II

THE SEPARATION AND DETERMINATION OF POTASSIUM AND SODIUM

KCl taken G.	KCl found G.	Error KCl G.	NaCl taken G.	NaCl found G.	Error NaCl G.
0.0083	0.0085	+0.0002	0.4256	0.4251	−0.0005
.0136	.0134	− .0002	.2545	.2550	+ .0005
.2024	.2017	− .0007	.2066	.2075	+ .0009
.0536	.0537	+ .0001	.1995	.1999	+ .0004
.1063	.1066	+ .0003	.1558[a]	.1567	+ .0009
.1012	.1006	− .0006	.1500	.1503	+ .0003
.1511	.1513	+ .0002	.1001	.1007	+ .0006
.2019	.2017	− .0002	.0550[a]	.0564	+ .0014
.2019	.2015	− .0004	.0505	.0512	+ .0007
.4010	.4001	− .0009	.0049	.0058	+ .0009

[a] These determinations are high because of an obvious contamination of the sodium sulfate during its recovery.

The use of 2 to 3 cc. of water to dissolve the mixed perchlorates of potassium and sodium followed by precipitation of the former by addition of butyl alcohol, requires more alcohol than the familiar extraction process. It was thought that the use of an excess of water over that required to dissolve sodium perchlorate and partially dissolve potassium perchlorate when present in large amount, would require the use of less alcohol without much decrease in accuracy as compared with the determinations listed in Table II. The determinations reported in Table III were made with 0.75

TABLE III

THE SEPARATION AND DETERMINATION OF POTASSIUM AND SODIUM BY A MODIFIED PROCEDURE USING LESS BUTYL ALCOHOL

KCl taken G.	KCl found G.	Error KCl G.	Filtrate and washings Cc.	NaCl taken G.	NaCl found G.	Error NaCl G.
0.4005	0.4000	−0.0004	53	0.0061	0.0067	+0.0006
.2010	.2009	− .0001	57	.0501	.0502	+ .0001
.1515	.1514	− .0001	55	.1000	.1004	+ .0004
.1028	.1026	− .0002	50	.1492	.1490	− .0002
.0506	.0509	+ .0003	47	.2001	...	.....
.0058	.0062	+ .0004	48	.2524	.2518	− .0006
.0094	.0099	+ .0005	53	.3998	...	...
.2004	.2006	+ .0002	57	.2019	.2017	− .0002

cc. of water and 25 cc. of butyl alcohol containing 0.5% of perchloric acid dihydrate to precipitate the potassium perchlorate, all other conditions being the same as previously described.

As will be seen from Table III results obtained using less alcohol, while not as good as those included in Table II, are still satisfactory.

Because of the low vapor pressure of butyl alcohol at water-bath temperatures, which must not be exceeded, direct determination of sodium as sulfate is comparatively slow and rather inconvenient. Since the determination of potassium is far more important than that of sodium, which is usually determined by difference following the determination of the mixed chlorides of potassium and sodium, and since by the method given the determination of potassium leaves nothing to be desired as to accuracy, the process is thought to be entirely adequate.

The correction for the solubility of potassium perchlorate to be applied in the absence of sodium was determined by precipitating 3 cc. of a saturated aqueous solution of potassium perchlorate in the manner already described, followed by filtration of the precipitated perchlorate and determination of the potassium in the filtrate. By duplicate analyses this correction was found to be 1.1 mg. of potassium perchlorate or 0.38 mg. of potassium oxide per 100 cc. of solution. This value is somewhat lower than that given in Table I but corresponds more exactly to working conditions.

The method as described has the following advantages: (1) absolute ethyl alcohol is replaced by *n*-butyl alcohol; (2) purification or dehydration of the alcohol used is not necessary; (3) it is a precipitation process; (4) one precipitation only is required; (5) the errors involved compensate one another exceptionally well.

A method has been devised by Willard and Smith[11] for the separation and determination of sodium and lithium using *n*-butyl alcohol. In this method butyl alcohol, used as received, was found adequate. The sodium was precipitated as chloride from its solution as perchlorate in butyl alcohol. The data described in the present paper indicate that butyl alcohol might be employed advantageously in an extraction process for the separation of potassium from sodium. Butyl alcohol could then be employed in the separation, successively, of potassium, sodium and lithium. The process is now being studied in this Laboratory.

The analyses reported in this paper include all of those carried out in the study of this method, with no omissions. The reliability of the process is thus demonstrated. No violent reactions were encountered throughout this work.

Summary

1. A method has been developed for the separation and determination of potassium and sodium depending upon the precipitation of potassium perchlorate from an aqueous solution by the addition of a comparatively

large volume of *n*-butyl alcohol, and its accuracy has been shown by its application to known mixtures of potassium and sodium chlorides.

2. The solubilities of potassium and sodium perchlorates in *n*-butyl alcohol have been determined.

3. The method was successfully applied in the separation and determination of known mixtures of potassium and sodium chloride including 20 determinations duplicating practical working conditions.

4. The method is particularly well adapted to the determination of potassium in the combined chlorides, the sodium being obtained by difference.

5. The use of *n*-butyl alcohol in proposed work on the separation and determination of potassium, sodium and lithium is discussed.

URBANA, ILLINOIS

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

THE HEATS OF VAPORIZATION OF MERCURY AND CADMIUM

BY MAYOR F. FOGLER[1] WITH WORTH H. RODEBUSH

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Probably the application of the quantum theory that is of most importance to physical chemists is the calculation of the entropies of the monatomic gases.[2,3] The expression[4,5] relating the vapor pressure of a monatomic liquid to its heat of vaporization also promises to be an application of considerable significance. While it is probable that the numerical results furnished by the quantum theory in these cases will be more exactly confirmed by more accurate data as in the case of other triumphs of the quantum theory, nevertheless there is always a danger in generalizing from meager or uncertain data.

The two elements that offer the best opportunity for a check upon the equation for the entropy of a monatomic gas are mercury and cadmium. The specific heats of these metals have been determined with considerable accuracy both for the solid and liquid, and the heats of fusion are known. There is, however, no direct determination of heat of vaporization of any metal described in the literature, that appears to be at all reliable. It is possible to calculate heat of vaporization from vapor-pressure data by means of the thermodynamic relation,

$$\frac{d\,ln\,p}{dT} = \frac{\Delta H}{RT^2} \qquad (1)$$

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[1] This communication is an abstract of a thesis submitted by M. F. Fogler in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Tolman, THIS JOURNAL, 42, 1185 (1920).

[3] Lewis, Gibson and Latimer, *ibid.*, 44, 1008 (1922).

[4] Dushman, *ibid.*, 43, 397 (1921).

[5] Rodebush, *ibid.*, 45, 606 (1923).