

lations of selenic acid are almost identical with those of sulfuric acid. Hence, accepting the estimates of Sherrill and Noyes¹ in the case of sulfuric acid as applicable to selenic acid, the statement may be made that selenic acid at a concentration 0.5 formal exists mainly in the form of the ions, H^+ and $HSeO_4^-$, whereas, at a concentration 0.01 formal, the ion $HSeO_4^-$ is about 67% dissociated into H^+ and SeO_4^{2-} ions. As the ionization constant of HSO_4^- was found to be 0.0115, that of $HSeO_4^-$ is of nearly the same magnitude.

Summary

The electromotive force of cells of the type, Pt, Quinhydrone H_2SO_4 (*c* formal), H_2SeO_4 (*c* formal) Quinhydrone, Pt, was measured at 25° and found to be substantially equal to zero over a range of acid concentration in the cell from 0.01 to 0.5 formal. At higher acid concentrations, 0.6 to 0.8 formal, reproducible results could not be obtained. The conclusion was drawn that in dilute solution the ionization relations of selenic acid are almost identical with those of sulfuric acid.

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AN EXTENSION OF THE ISOAMYL ALCOHOL SEPARATION OF THE ALKALI AND ALKALINE EARTH METALS TO THE LESS COMMON ALKALIES, LITHIUM, RUBIDIUM AND CESIUM

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Gooch has shown that isoamyl alcohol can be applied to the quantitative separation of lithium from sodium and potassium by its solvent action upon the chlorides,² and Browning has used the same alcohol for bringing about a separation of calcium from barium and strontium using the nitrates³ and of strontium from barium using the bromides.⁴ Detailed schemes for the qualitative analysis of the entire alkali group have been developed by Ato and Wada,⁵ and Noyes and Bray.⁶ These methods were designed to detect small quantities of any one of the alkalies when present in admixture with large amounts of the others. Because of the similar solubilities of the salts of potassium, rubidium and cesium, the

¹ Formerly a fellow at the University.

² F. A. Gooch. *Am. Chem. J.*, **9**, 33 (1887).

³ P. E. Browning. *Am. J. Sci.*, **43**, 50 and 314 (1892).

⁴ P. E. Browning, *ibid.*, **44**, 459 (1892).

⁵ Sunao Ato and Isaburo Wada, *Sci. Papers Inst. Phys. Chem. Research*, **4**, 261 (1926), in English; *Z. anal. Chem.*, **72**, 50 (1927).

⁶ Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," 1927. p. 246.

procedures are lengthy, involve the use of uncommon reagents, and demand considerable skill and experience from the analyst. In view of their researches, it is doubtful whether a simple scheme of ion analysis can be devised for the general mixture of alkalies.

In a previous paper⁷ I have extended the application of isoamyl alcohol to the qualitative analysis of the common alkali and alkaline earth metals by a primary division of the bromide salts into two groups. It was thought advisable to study the distribution of lithium, rubidium and cesium bromides when the mixture, together with the salts of the common alkali and alkaline earths, was treated with the solvent in order to determine how their presence would conflict with the detection of the common elements; and if it were possible to effect a simple separation of the rare alkalies therewith.

Measurements of the solubility of the rare alkali bromides revealed that the lithium salt was very soluble, but that only 0.05 and 0.06 mg. of the respective rubidium and cesium bromides dissolved in 1 cc. of isoamyl alcohol at 25°. Lithium was found to accompany the members of the soluble group, magnesium, calcium and strontium, whereas rubidium and cesium, when present in appreciable amounts, separated with the sodium, barium and potassium bromides. The separation into two groups, as described in the first paper, involved the extraction of the anhydrous bromides with isoamyl alcohol. It was found more satisfactory to dissolve the salts in a minimum of water, and to cause the precipitation of the insoluble group by boiling the solution with an excess of isoamyl alcohol until the water was expelled (1). Experiments showed that this caused the precipitation of 1 mg. of all the insoluble bromides and kept in solution 300 mg. of lithium, calcium and magnesium bromides, but only 100 mg. of the strontium salt.

The presence of lithium in the soluble group does not materially alter the procedure for the separation and detection of calcium and magnesium. In the separation of strontium from calcium by the action of 16 *N* nitric acid, it was found that when large quantities of lithium were present, small quantities of the nitrate remained behind with the strontium. This makes a further confirmatory test for strontium desirable (2). Lithium is detected in the filtrate, after the usual separation of calcium as the oxalate, by precipitation of lithium stearate from an isoamyl alcohol solution (3). By using the nitrate salts, instead of the chlorides as recommended by Caley,⁸ traces of strontium do not confuse the test for lithium because strontium nitrate is not extracted by the isoamyl alcohol.

The first step in the analysis of the insoluble group of bromides is to boil the mixture with 1-2 cc. of 95% ethyl alcohol containing 1-2 drops

⁷ H. Yagoda, *THIS JOURNAL*, **52**, 3068 (1930).

⁸ E. R. Caley, *ibid.*, **52**, 2754 (1930).

of 8 *N* hydrobromic acid. The solubilities of rubidium and cesium bromides in this medium at 25° are 1.8 and 2.1 mg. per cc., respectively. When the volume of the solvent is 2 cc. quantities of the rare alkalies in excess of 1 mg. each will accompany the potassium in the insoluble sub-group. On addition of 12 *N* hydrochloric acid to the soluble sub-group, sodium and barium chlorides precipitate, the traces of potassium, rubidium and cesium chlorides remaining dissolved. The sodium and barium chlorides are filtered off and washed with 12 *N* hydrochloric acid (4). The filtrate is combined with the solution obtained by dissolving the insoluble sub-group in 5 cc. of hot water. The combined liquid is freed from alcohol and acid by evaporation to dryness, the residue is redissolved in 5 cc. of water, the solution precipitated with sodium cobaltinitrite reagent and filtered. This yellow precipitate consists, in general, of potassium, rubidium and cesium cobaltinitrites. The presence or absence of the rare alkalies is best ascertained by spectroscopic analysis of the flame spectrum. If a knowledge of their relative quantities is desired, the cobaltinitrite mixture can be separated by following procedure 166 as described by Noyes and Bray.⁹

Notes on the Procedure

(1) The mixed bromides taken for analysis should not exceed 100 mg. in weight. Add hot water dropwise until it just dissolves, then add 10 cc. of isoamyl alcohol, boil down to a volume of 2 cc., add 1 drop of 8 *N* hydrobromic acid and 1 cc. of the cold solvent, cool, filter and wash the precipitate with about 1 cc. of isoamyl alcohol. In order that the liquid may boil quietly when water is present in the solvent, a stirring rod terminating in a capillary tip is placed in the beaker. The rod is made by drawing out a 4-mm. glass tube to a coarse capillary of total length 10 cm. and sealing a solid constriction in the glass about 1 cm. from the capillary end.

(2) The salt insoluble in the nitric acid is filtered off, dried by air suction, redissolved in 0.5 cc. of water, and the solution is boiled with 5 cc. of isoamyl alcohol until the volume is reduced to 2 cc. If strontium is present, strontium nitrate will precipitate out.¹⁰ Both lithium and calcium nitrates are soluble in isoamyl alcohol.

(3) Evaporate the filtrate from the calcium oxalate to dryness, add 1 cc. of 16 *N* nitric acid, heat until excess ammonium oxalate is decomposed, cool, add 2-3 cc. of isoamyl alcohol, boil, cool and filter into a 10-cc. test-tube. To the filtrate add 2.5 times its volume of a freshly prepared 2% solution of ammonium stearate in isoamyl alcohol. A white precipitate forming is lithium stearate.

(4) The chlorides of sodium and barium are examined in the flame. If the color reveals the presence of both, dissolve the salts in 2 cc. of water, add a few drops of 6 *N* sulfuric acid, boil, cool and filter off any barium sulfate formed. Sodium is detected in the filtrate by the addition of 1 cc. of ethyl alcohol and 3 cc. of zinc uranyl acetate reagent, a greenish-yellow crystalline precipitate forms. This reagent, developed by Kolthoff,¹¹ consists of 10 g. of $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$, 30 g. of $\text{ZnAc}_2 \cdot 3\text{H}_2\text{O}$, 9 g. of 30% acetic

⁹ Ref. 6, p. 260.

¹⁰ P. E. Browning, *Am. J. Sci.*, **43**, 387 (1892).

¹¹ H. H. Barber and I. M. Kolthoff, *THIS JOURNAL*, **50**, 1625 (1928); I. M. Kolthoff, *Z. anal. Chem.*, **70**, 397 (1926).

acid and 130 g. of water; the two salts are dissolved separately in equal volumes of water, the acid is added and the mixture filtered.

IDENTIFICATION OF THE ALKALI AND ALKALINE EARTH METALS

Concentrate filtrate from the 3d analytical group down to 5 cc. Transfer to a 30-cc. beaker, add 3 cc. of 16 *N* HNO₃ and evaporate to dryness. Add 2 cc. of 8 *N* HBr, boil off acid and cool dry residue. If this is large, dissolve only a 100-mg. portion in a minimum of hot water, add 10 cc. of isoamyl alcohol, boil down to a volume of 2 cc., add 1 drop of 8 *N* HBr and 1 cc. of isoamyl alcohol, cool, filter and wash precipitate with small volume of solvent.

ANALYSIS OF PRECIPITATE

Precipitate: NaBr, BaBr₂, KBr, RbBr and CsBr. Make flame test. Boil dry residue with 2 cc. of 95% ethyl alcohol, add 2 drops of 8 *N* HBr, cool and filter.

<i>Precipitate:</i> Chiefly K, Rb and Cs bromides. Wash with 1 cc. of 95% ethyl alcohol. Dissolve in 5 cc. of hot water.	<i>Filtrate:</i> Contains NaBr, BaBr ₂ and traces of KBr, RbBr and CsBr. Add 0.5 cc. of 12 <i>N</i> HCl dropwise, cool and filter.
	<i>Precipitate:</i> NaCl and BaCl ₂ . Dissolve in 2 cc. of water, add a few drops of 6 <i>N</i> H ₂ SO ₄ , boil and filter. A white precipitate is BaSO ₄ . To the filtrate add 1 cc. of 95% ethyl alcohol and 3 cc. of zinc uranyl acetate reagent. A greenish-yellow precipitate confirms presence of sodium.
	<i>Filtrate:</i> RbCl, CsCl and KCl. Evaporate to dryness. Combine with main portion of bromide salts. Add a 25% solution of Na ₂ Co(NO ₂) ₆ dropwise, filter, wash with 50% ethyl alcohol. Examine spectroscopically.

ANALYSIS OF FILTRATE

Filtrate: MgBr₂, SrBr₂, CaBr₂ and LiBr. Boil off the isoamyl alcohol, add 1 cc. of 16 *N* HNO₃ and evaporate to dryness. *Residue:* Mg(NO₃)₂, Ca(NO₃)₂, Sr(NO₃)₂ and LiNO₃. Heat strongly, cool, add 3 cc. of water, boil and filter.

<i>Residue:</i> MgO and Mg(OH) ₂ . Redissolve in 1 cc. of 6 <i>N</i> HCl, add 1 cc. of 1 <i>N</i> (NH ₄) ₂ HPO ₄ and 2 cc. of 16 <i>N</i> NH ₄ OH. A white crystalline precipitate of MgNH ₄ PO ₄ confirms presence of magnesium.	<i>Filtrate:</i> Sr(NO ₃) ₂ , Ca(NO ₃) ₂ and LiNO ₃ . Evaporate to dryness, cool, add 1 cc. of 16 <i>N</i> HNO ₃ , raise to a boil, add another 1-cc. portion of acid, cool and filter, moistening paper with nitric acid and using suction.
	<i>Precipitate:</i> Sr(NO ₃) ₂ . Dry, dissolve in 0.5 cc. of hot water, add 5 cc. of isoamyl alcohol, boil until volume is 2 cc. The appearance of a white precipitate confirms presence of strontium.
	<i>Filtrate:</i> Ca(NO ₃) ₂ and LiNO ₃ . Boil off excess acid, redissolve in 3 cc. of water, make ammoniacal, add 1 cc. of saturated (NH ₄) ₂ C ₂ O ₄ solution. A white precipitate confirms calcium.
	Filter, evaporate filtrate to dryness, heat until excess oxalate is volatilized, cool, add 2 cc. of isoamyl alcohol, boil, cool and filter. To filtrate add 5 cc. of a freshly prepared 2% ammonium stearate solution in isoamyl alcohol. A white precipitate is lithium stearate.

Summary

In the qualitative analysis for all the alkali and alkaline earth metals, isoamyl alcohol acting on a mixture of the bromides effects a primary separation of the elements into two groups. The soluble group consists of magnesium, strontium, calcium and lithium bromides; it is further separated by simple methods involving the specific behavior of the nitrates upon ignition, solution in nitric acid and precipitation from isoamyl alcohol solution. The insoluble group, consisting of sodium, barium,

potassium, rubidium and cesium bromides, is treated as described in a previous paper, the rare alkalis being provided for by segregating them into one group along with potassium. The procedure, based on quantitative separations of the individual elements, has been tested and found satisfactory for a rapid identification of the alkali and alkaline earth metals when present in mixture.

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THE NATURE OF THE CHEMICAL BOND. III. THE TRANSITION FROM ONE EXTREME BOND TYPE TO ANOTHER¹

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A question which has been keenly argued for a number of years is the following: if it were possible continuously to vary one or more of the parameters determining the nature of a system such as a molecule or a crystal, say the effective nuclear charges, then would the transition from one extreme bond type to another take place continuously, or would it show discontinuities? For example, are there possible all intermediate bond types between the pure ionic bond and the pure electron-pair bond? With the development of our knowledge of the nature of the chemical bond it has become evident that this question and others like it cannot be answered categorically. It is necessary to define the terms used and to indicate the point of view adopted; and then it may turn out, as with this question, that no statement of universal application can be made.

In the following sections, after a discussion of the properties of ionic compounds and compounds containing electron-pair bonds, the transition from one extreme to the other is considered. It is concluded that in some cases the transition could take place continuously, whereas in others an effective discontinuity would appear.

Bond Type and Atomic Arrangement

The properties of a compound depend on two main factors, the nature of the bonds between the atoms, and the nature of the atomic arrangement. It is convenient to consider that actual bonds approach more or less closely one or another of certain postulated extreme bond types (ionic, electron-pair, ion-dipole, one-electron, three-electron, metallic, etc.), or

¹ A part of the material of this paper was presented to the American Chemical Society at Buffalo, New York, September 2, 1931, under the title "The Structure of Crystals and the Nature of the Chemical Bond."