addition of calcium oxide to form the series $CaSiO_3$, Ca_2SiO_4 and Ca_3SiO_5. Torgeson and Sahama[2] obtained $\Delta H_{298.16} = -21{,}250$ for the first step, $CaO + SiO_2$ (quartz) = $CaSiO_3$ (wollastonite). For $CaO + CaSiO_3$ (wollastonite) = $Ca_2SiO_4(\beta)$, $\Delta H_{298.16} = -8{,}940$; and for $CaO + Ca_2SiO_4(\beta) = Ca_3SiO_5$, $\Delta H_{298.16} = 3{,}210$. The heat of the last step is positive and, as the entropy change would be expected to be quite small, tricalcium silicate evidently is unstable with respect to orthosilicate and calcium oxide at 298.16°K.

Summary

Measurements were made of the heats of reaction of calcium orthosilicate, tricalcium silicate, zinc orthosilicate, calcium oxide, zinc oxide and quartz with hydrofluoric acid.

The heats of formation of the silicates from the oxides were obtained as follows: $Ca_2SiO_4(\beta)$, $\Delta H_{298.16} = -30{,}190 \pm 230$; Ca_3SiO_5, $\Delta H_{298.16} = -26{,}980 \pm 220$; and Zn_2SiO_4 (willemite), $\Delta H_{298.16} = -6{,}990 \pm 140$ cal./mole.

BERKELEY, CALIFORNIA RECEIVED AUGUST 2, 1950

[CONTRIBUTION NO. 95 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Salts of Perrhenic Acid. IV. The Group II Cations, Copper(II) and Lead(II)[1]

BY WILLIAM T. SMITH, JR., AND GROVER E. MAXWELL

All of these salts except the perrhenates of beryllium and mercury(II) have been previously reported.[2,3] However, the only property reported was composition, and no definite conclusions concerning degree of hydration were drawn.

Preparation of the Salts.—In most cases the hydroxide, oxide or carbonate of the metal was treated with a solution of perrhenic acid[4] and the hydrated salt was crystallized by evaporating the solution at room temperature over calcium chloride. Beryllium perrhenate was prepared by treating the metal with perrhenic acid and hydrogen peroxide and warming the mixture. The first attempt resulted in a solution which contained a considerable excess of beryllium. Presumably, a soluble, basic beryllium perrhenate was obtained. An excess of perrhenic acid was used in a subsequent preparation of this salt. Mercury(II) perrhenate was prepared from mercury(II) oxide and perrhenic acid. An insoluble basic salt was produced. The normal salt was obtained by recrystallization from water containing an excess of perrhenic acid.

Hydrates.—The hydrates which separated from water solution at room temperature are listed in Table I. Strontium perrhenate monohydrate was the only lower hydrate isolated.

In most cases the water of hydration was determined from weight lost on dehydration. Most of the hydrates were stable enough so that well formed crystals could be air dried at ordinary indoor temperatures and humidities during winter. The hydrates of the perrhenates of zinc, cadmium, and copper(II) were deliquescent under these conditions, and the dehydration data were inconclusive. A satisfactory characterization was effected by noting the weight gained as the salts became hydrated over 60% sulfuric acid. The study of beryllium perrhenate dihydrate was discontinued, due to the health hazard involved,[5] before a satisfactory characterization was made. The agreement of the water found with the calculated value shown in Table I is possibly fortuitous since this value is the average of two divergent determinations, 6.09 and 7.16%. Strontium perrhenate monohydrate was formed when the dihydrate was exposed to the ambient air. The monohydrate was stable over calcium chloride and was dehydrated by heating in an oven at 105°. The dehydration curves gave no indication of lower hydrates for the other salts. Barium perrhenate tetrahydrate and lead(II) perrhenate dihydrate were completely dehydrated when exposed to the ambient air. All of the other hydrates, with the exception of strontium perrhenate dihydrate, were completely dehydrated over calcium chloride. Completeness of dehydration was verified by either igniting the anhydrous residues at 600° or by analyzing them for perrhenate and the cation.

Analysis of the Salts.—All analyses were run in duplicate and good precision was obtained. Standard analytical methods were satisfactory for a majority of the salts, but in some cases it was necessary to develop special procedures. For the determination of perrhenate, a modification of the method of Willard and Smith[6] was directly applicable to all but the perrhenates of zinc, cadmium, mercury(II) and lead(II). Lead was removed as the sulfate to prevent the precipitation of lead(II) chloride when tetraphenylarsonium chloride was added. Zinc and cadmium were removed and determined as 8-hydroxyquinolates. Their removal was necessary since they form precipitates with tetraphenylarsonium chloride.[7] Tests on standard samples revealed that the excess 8-hydroxyquinoline in the filtrate from the cation determinations did not interfere with the perrhenate determination.

Attempts to remove mercury quantitatively as the 8-hydroxyquinolate were unsuccessful. Simultaneous precipitation of mercury(II) with tetraphenylarsonium chloride, suggested by a similar procedure developed for thallium(I) perrhenate,[8] was unsatisfactory since no wash liquid was found which did not dissolve the mercury precipitate. In

---

[1] This paper is based on a dissertation presented by Grover E. Maxwell to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the Ph.D. degree, June, 1950.

[2] Wilke-Dorfurt and Gunzert, *Z. anorg. allgem. Chem.*, **215**, 369 (1933).

[3] Briscoe, Robinson and Rudge, *J. Chem. Soc.*, 2211 (1931).

[4] Smith and Maxwell, THIS JOURNAL, **71**, 578 (1949).

[5] Stokinger, *Nucleonics*, **5**, No. 6, 53 (1949).

[6] Willard and Smith, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 305 (1939).

[7] Willard and Smith, *ibid.*, **11**, 269 (1939).

[8] Smith, *Anal. Chem.*, **20**, 937 (1948).

TABLE I

PROPERTIES OF THE PERRHENATES

Compound	Composition, %		Soly., g./100 g. H_2O			F.p., °C.	Transition point, °C.	Density g./cc. at approx. 25°C.
	Found	Calcd.	0°	30°	50°			
$Be(ReO_4)_2$	Be, 1.59	1.77						
	ReO_4, 92.0	98.2						
$Be(ReO_4)_2 \cdot 2H_2O$	H_2O, 6.63	6.60						
$Mg(ReO_4)_2$	Mg, 4.65	4.63		283.6		930		5.01
	ReO_4, 95.3	95.4						
$Mg(ReO_4)_2 \cdot 4H_2O$[a]	H_2O, 12.5	12.1		527.7				3.51
$Ca(ReO_4)_2$	Ca, 7.39	7.41		187.0		934	778	4.94
	ReO_4, 92.8	92.6						
$Ca(ReO_4)_2 \cdot 2H_2O$[b]	H_2O, 6.26	6.24		227.8				4.45
$Sr(ReO_4)_2$	Sr, 14.86	14.90		110.1		884	788	4.95
	ReO_4, 85.0	85.1						
$Sr(ReO_4)_2 \cdot H_2O$	H_2O, 2.94	2.97		117.5				
$Sr(ReO_4)_2 \cdot 2H_2O$[c]	H_2O, 5.65	5.79		125.3				4.82
$Ba(ReO_4)_2$	Ba, 21.44	21.53	1.52	8.13	21.51	799		5.91
	ReO_4, 71.3	71.5						
$Ba(ReO_4)_2 \cdot 4H_2O$[d]	H_2O, 10.4	10.7	1.69	9.13	24.54			4.13
$Zn(ReO_4)_2$	Zn, 11.54	11.55		313.6		701		5.46
	ReO_4, 88.6	88.5						
$Zn(ReO_4)_2 \cdot 4H_2O$[e]	H_2O, 11.24	11.29		588.4				3.75
$Cd(ReO_4)_2$	Cd, 18.16	18.33		497.5		624		5.99
	ReO_4, 81.3	81.7						
$Cd(ReO_4)_2 \cdot 2H_2O$[f]	H_2O, 5.77	5.56		743.9				4.95
$Hg(ReO_4)_2$	Hg, 28.24	28.62				431	405	6.95
	ReO_4, 73.7	71.4						
$Hg(ReO_4)_2 \cdot 2H_2O$	H_2O, 4.94	4.89						5.62
$Cu(ReO_4)_2$				210.4				
$Cu(ReO_4)_2 \cdot 4H_2O$[g]	Cu, 9.83	9.99		324.5				3.73
	ReO_4, 78.1	78.7						
	H_2O, 11.34	11.33						
$Pb(ReO_4)_2$[h]	Pb, 29.22	29.27	4.14	14.81	29.63	562		6.93
	ReO_4, 71.1	70.7						
$Pb(ReO_4)_2 \cdot 2H_2O$	H_2O, 4.83	4.84	4.36	15.67	31.61			5.16

[a] Wilke-Dorfurt and Gunzert[2] reported that this compound is either the pentahydrate or tetrahydrate. [b] These authors[2] assigned the formula, $Ca(ReO_4)_2 \cdot 2^1/_2H_2O$, to this hydrate. [c] This compound has been previously reported.[2] [d] The Noddacks reported the isolation of barium perrhenate dihydrate.[2] [e] Wilke-Dorfurt and Gunzert[2] believed this compound to be the hexahydrate. [f] This compound has been reported to be a trihydrate [2] [g] The pentahydrate[3] and hexahydrate[2] of copper(II) perrhenate have been reported. [h] Wilke-Dorfurt and Gunzert[2] reported that their attempts to prepare lead(II) perrhenate resulted in the formation of a basic salt.

the method finally adopted the mercury was partially removed as mercury(II) oxide formed by the addition of sodium hydroxide. Exploratory experiments revealed that if the filtrate was neutralized with hydrochloric acid enough mercury remained to give a precipitate with tetraphenylarsonium chloride. However, when the solution was made alkaline with ammonium hydroxide no precipitation occurred. When the method was applied to standard samples excellent results were obtained, but in subsequent analyses a small amount of a white precipitate, presumably $HgNH_2Cl$, was formed. Although this was removed by filtration, the analytical results were usually higher than was expected, and it seems probable that some of the residual mercury was post-precipitated. The analytical data are given in Table I.

Solubilities.—The method used for determination of the solubilities has been described by Smith and Long.[9] The measurements were made at 30 ± 0.03°. In addition, the solubilities of barium perrhenate tetrahydrate and lead(II) perrhenate dihydrate were determined at 0 and 50° to provide data from which the heats of solution could be calculated. This was not done for the other salts because of their extremely high solubilities. It was not possible to measure the solubility of mercury(II) perrhenate since this compound is decomposed by water. All determinations were made in duplicate, approaching equilibrium both from above and from below equilibrium concentrations, and a precision of about five parts in a thousand was obtained. The solubilities of the anhydrous salts and of strontium perrhenate monohydrate were calculated from the measured solubilities of the hydrates which were in equilibrium with the saturated solutions. With the perrhenates of the alkaline earth cations there is a marked decrease in solubility with increasing atomic number. With the zinc and cadmium salts this trend is reversed.

Heats of Solution.—The logarithm of the solubility was plotted against the reciprocal of the absolute temperature for barium perrhenate tetrahydrate and lead(II) perrhenate dihydrate. The heats of solution, obtained from the slopes of the curves, were 9.46 kcal. per mole for the barium salt and 6.95 kcal. per mole for the lead compound.

---

(9) Smith and Long, THIS JOURNAL, **70**, 354 (1948).

Good straight lines were obtained in both cases, indicating that the heats of solution are constant in the temperature range from 0 to 50°.

Densities and Molar Volumes.—The method used for density determinations has been described previously.[4] Since anhydrous copper(II) perrhenate and strontium perrhenate monohydrate could not be prepared by primary crystallization, their densities were not determined. It is of interest to note that all of the tetrahydrates have the same molar volume, 171 ± 1 cc., and that the molar volumes of the dihydrates, with the exception of those of mercury(II) perrhenate and lead(II) perrhenate, all amount to 130 ± 1 cc. The molar volumes of the two exceptions are 135 and 144 cc., respectively. The similarity of molar volumes probably indicates that the crystal structures are identical and that the critical factors are the sizes of the anions, the cations being contained in the interstices. With the anhydrous salts the molar volumes increase from 105 cc. for magnesium perrhenate to 109 cc. for calcium perrhenate and 119 cc. for strontium perrhenate. There is then a sharp decrease to 108 cc. for barium perrhenate. The fact that the solid perrhenates of calcium and strontium undergo a transition above room temperature may account for the anomalous molar volumes. The molar volumes of the perrhenates of the zinc family cations and of lead(II) perrhenate all amounted to 102 ± 2 cc. Here again, identical crystal structures, with anion–anion contact, seem to be indicated.

Freezing Points.—The method used for freezing point determinations has been described in a previous paper.[4] The salts with freezing points above 700° were fused in a platinum test-tube, and the thermocouple was wrapped in platinum foil. Copper(II) perrhenate decomposed below the melting point. In general the freezing points decrease with increasing cation size. This is expected since, other factors being equal, crystals with small cations have higher lattice energies.

Transition Points.—Three of the salts, the perrhenates of calcium, strontium, and mercury(II), were found to have solid transition points, as evidenced by two inflection points in the cooling curves. The fact that analysis had shown the salts to be quite pure and that there was no indication of decomposition when the salts were fused seems to rule out the possibility that the second inflection point was due to the presence of impurities. The melting point of mercury(II) perrhenate was low enough to permit its fusion in a glass tube so that its transition point could be observed visually. The clear, orange colored melt solidified to form a light yellow, translucent solid. Presently, this was transformed into a white opaque solid at the top of the melt and at the bottom of the tube. The lines of demarcation separating the two forms were sharp and distinct. They moved slowly toward the middle of the sample until the entire mass was transformed into the low temperature form.

Microscopic Examination of Crystals.—All of the salts which were obtained by primary crystallization either from water solution or from the fused salts were examined in polarized light with a microscope. They were all anisotropic.

Summary

The perrhenates of the Group II cations of the Periodic Chart and of copper(II) and lead(II) were prepared, and some of their properties were studied. The examination of beryllium perrhenate was discontinued due to the health hazard involved. The compounds which separated from water solution at room temperature were the tetrahydrates of the perrhenates of magnesium, barium, zinc and copper(II), and the dihydrates of the perrhenates of beryllium, calcium, strontium, cadmium, mercury(II) and lead(II). The monohydrate of strontium perrhenate was also isolated. Analyses indicated that the salts had the expected compositions and were satisfactorily pure. All of the compounds are colorless or white with the exception of copper (II) perrhenate tetrahydrate which is blue and the high temperature form of mercury(II) perrhenate which is light yellow. Data on the freezing points, solubilities, densities and optical properties were obtained. The heats of solution of barium perrhenate tetrahydrate and lead(II) perrhenate dihydrate were also determined.

KNOXVILLE, TENN. RECEIVED AUGUST 7, 1950