The Preparation, Aqueous and Perchloric Acid Solubilities, Solution Densities and Transition Temperature of Silver Perchlorate

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Introduction

Saturated aqueous solutions of silver perchlorate are of interest because of their high density. We have therefore repeated and confirmed the determination by Hill[1] of the solubility of this substance in water and have in addition determined the solubility of the anhydrous salt in various concentrations of perchloric acid. Our procedure was practically identical with that followed by Hill except that the density determinations were somewhat refined by the use of a 25-ml. pycnometer.

Preparation of Silver Perchlorate.—The anhydrous salt is prepared easily by heating silver nitrate with a large excess of 72% perchloric acid on a hot plate until the nitric acid is driven off and copious fumes of perchloric acid are evolved. The resultant mixture of crystals and mother liquor is then cooled at 0°, centrifuged, and most of the adhering perchloric acid removed by drying at 150° in a vacuum. The mother liquors may be used for the conversion of another portion of silver nitrate.

Some silver chloride is formed during the above process and appreciable quantities of it remain dissolved in the concentrated solution of silver perchlorate and will precipitate on dilution. To remove this the silver perchlorate is dissolved in water, the solution neutralized with a slight excess of silver carbonate or oxide, filtered, evaporated on a hot-plate, cooled, and the resultant crystalline hydrate, $AgClO_4 \cdot H_2O$, centrifuged. The filtrate, fortified by the addition of the solid phase in sufficient amount to provide an excess at any specified temperature, is used for the solubility determinations.

Anhydrous silver perchlorate is very deliquescent and should be stored in open dishes in a large desiccator over anhydrous magnesium perchlorate in the dark. It is not light sensitive when slightly acid with perchloric acid, but becomes so when the acid is removed completely.

The Aqueous Solubility and Density Determinations.—The range 0–35° was repeated with the usual solubility measurements, the solutions being analyzed by Volhard's method and the densities determined by use of a 25-ml. pycnometer. The results are given in Table I and are shown graphically in Fig. 1.

TABLE I

THE SOLUBILITY AND DENSITY OF AQUEOUS SOLUTIONS OF SILVER PERCHLORATE MONOHYDRATE IN THE TEMPERATURE RANGE 0–35°

Temp., °C.	Sp. gr. vac. corr. Temp./4°	$AgClO_4$ solubility, %	A. E. Hill's Detn.[1] $AgClO_4$ soly., %	Sp. gr. Temp./4°
0	2.7251	82.07	81.30	2.667
10	2.7594	82.88	...	...
20	2.8163	84.04	...	...
25	2.8487	84.78	84.50	2.806
30	2.8825	85.59	...	...
35	2.9173	86.21	...	...

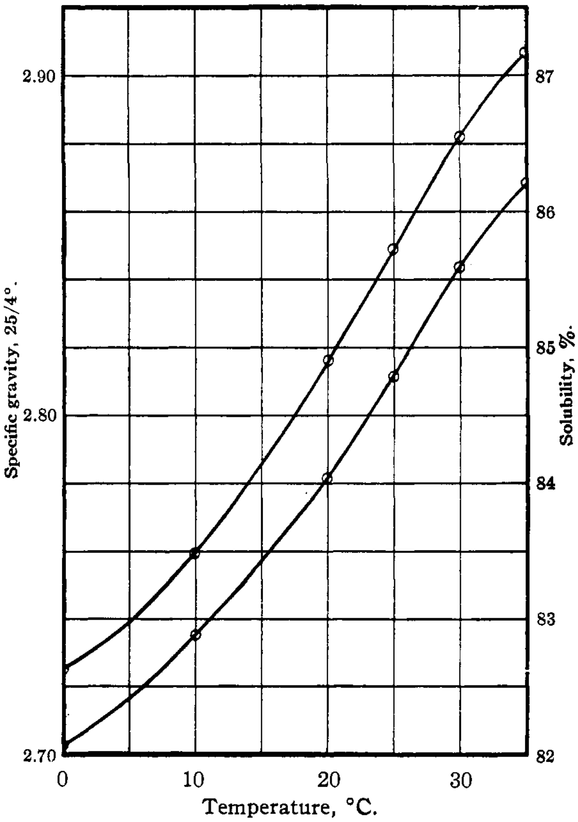

Fig. 1.—Solubility and solution density of saturated aqueous solutions at 0–35°: upper curve, specific gravity; lower curve, solubility.

One thousand ml. of saturated aqueous silver perchlorate solution at 25° contains 2415 g. of silver perchlorate; 100 g. of water dissolves 557 g. of silver perchlorate at 25°. The values given by Hill[1] are 2368 and 540, respectively.

An attempt to fortify a saturated solution of silver perchlorate by the addition of silver chloride to increase density resulted in but a slight increase in value. A saturated solution of silver perchlorate at 25° was stirred with an excess of lead perchlorate, $PbOHClO_4$, and the result was a diminution in density from 2.8478 to 2.8290.

The refractive index of the saturated silver perchlorate solutions as determined by using an Abbé refractometer at 15 to 35° are shown in Fig. 2. The viscosity of these solutions is somewhat less than that of Thoulet's solution of comparable density. A material advantage of silver perchlorate solutions over Thoulet's solution is that they do not have the hazard from mercury poisoning. Silver

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(1) Hill, THIS JOURNAL, **44**, 1163 (1922).

perchlorate is, however, troublesome because of its corrosive nature in contact with the skin.

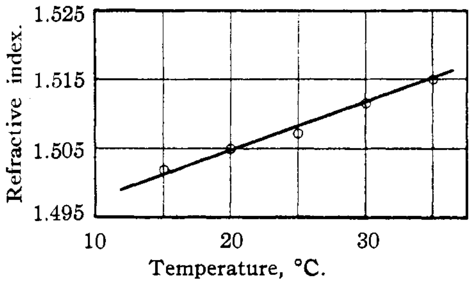

Fig. 2.—Refractive index of saturated silver perchlorate solutions at 15–35°.

The value of Hill for the transition temperature of silver perchlorate monohydrate to the anhydrous salt (43.1°) was checked in the usual manner and the authors find the value 43.0°.

TABLE II

THE SOLUBILITY AND SOLUTION DENSITY OF ANHYDROUS SILVER PERCHLORATE IN 60–73.6% PERCHLORIC ACID AT 25 AND 0°

Temp., °C.	Acid concn., %	Solubility, g. $AgClO_4$ per 100 ml. sol.	Solubility, g. $AgClO_4$ per 100 g. of sol.	Density 25/4°	Density 0/4°
25	73.60	5.252	3.011	1.7436	....
25	68.02	10.332	6.080	1.6993	....
25	64.08	20.080	11.765	1.7066	....
25	60.00	38.449	21.611	1.7790	....
0	73.60	3.754	2.136	....	1.7575
0	68.08	7.104	4.151	....	1.7107
0	64.31	13.478	7.931	....	1.6987
0	60.16	30.500	17.41	....	1.7520

Perchloric Acid Solubility of Anhydrous Silver Perchlorate.—The solubility determinations in strong perchloric acid and the density determinations of these solutions were carried out as previously described for the aqueous solutions. Anhydrous silver perchlorate was used as solute. The constant boiling perchloric acid (73.60% $HClO_4$) was prepared by the Smith and Koch method.[2] More dilute solutions of perchloric acid were made from this product by weight dilution. The data for the perchloric acid solubilities and solution densities are given in Table II.

Summary

1. A redetermination of the solubility of silver perchlorate in the temperature range 0–35° has been made. The previously reported data by Hill[1] and the present data were found to be in substantial agreement.

2. The refractive index of saturated aqueous solutions of silver perchlorate over the temperature range 15–35° has been given.

3. The solubility of anhydrous silver perchlorate in strong perchloric acid (60–73.6%) at 0 and 25° has been determined. Solution densities are also given.

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[2] Smith and Koch, *Ind. Eng. Chem., Anal. Ed.*, **3**, 52 (1931).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Activity and Osmotic Coefficients of Some Hydroxide–Chloride Mixtures in Aqueous Solution

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The cells

$$\mathrm{H_2} \mid \mathrm{MOH}(m_1),\ \mathrm{MX}(m_2) \mid \mathrm{M}_x\mathrm{Hg} \mid \mathrm{MOH}(m_0) \mid \mathrm{H_2} \qquad (1)$$

and

$$\mathrm{Ag{-}AgX} \mid \mathrm{MOH}(m_1),\ \mathrm{MX}(m_2) \mid \mathrm{M}_x\mathrm{Hg} \mid \mathrm{MX}(m_0') \mid \mathrm{AgX{-}Ag} \qquad (2)$$

in which X equals Cl, Br, are peculiarly adapted for the study of hydroxide–halide mixtures since by the first the activity coefficient of the hydroxide and by the second the activity coefficient of the halide may be evaluated in a given mixture. The first of these cells has been employed[1–4] for determining the activity coefficient of a hydroxide in a halide solution, but measurements of both cells have never been used before for the determination of the activity coefficients of both electrolytic components in the mixtures.

We have restricted this study to the investigation of sodium and potassium hydroxide–chloride mixtures in water at 25° at constant total molalities of 0.5 and 1 *M*. As shown by Harned and Harris, Jr.,[4] the hydroxide–chloride mixtures differ from other mixtures of strong uni-univalent electrolytes in that the logarithm of the activity coefficients of the hydroxide does not vary linearly with the hydroxide concentration at constant total molality. Our results will be shown to confirm this observation. Further, since the measurements of both cells lead to the

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(1) Harned, THIS JOURNAL, **47**, 684, 689 (1925).

(2) Harned and Swindells, *ibid.*, **48**, 126 (1926).

(3) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

(4) Harned and Harris, Jr., THIS JOURNAL, **50**, 2633 (1928).