

oxygen excluded, as that of Roberts and Fenwick, will give higher potentials.

Summary

1. The use of a vacuum-tube potentiometer with stick antimony electrodes eliminates drifting of the potential and gives rapid, constant and reproducible readings.

2. Stirring of a solution or the bubbling of a gas through it causes a deviation of the values away from the theoretical.

3. The stick antimony electrode in an unstirred solution in contact with air at equilibrium with both antimony and antimony trioxide gives a correct measurement of P_H values from P_H 2 to 7 inclusive. The value of E with this electrode measured against the normal calomel electrode is obtained by the equation $E = +0.030 + 0.5915 P_H$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]
**PHOTOMETRIC DETERMINATION OF THE SOLUBILITY OF
SILVER CHLORIDE AND OF MERCUROUS CHLORIDE¹**

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Introduction

Utilization of the Tyndall beam in the determination of the amount of suspended material in dispersed systems has often been attempted. As pointed out by Wells,³ the phenomena encountered are extremely complex. Turbidity is doubtless a measure of other factors beside concentration. In spite of such limitations, methods employing the Tyndall beam possess certain attractive features, one of the most significant of which is that of extreme sensitivity.

Nephelometric analysis, employing the comparison of intensity of light reflected by a suspension of unknown concentration with that from a suspension of the same substance of known concentration, is a convenient method for the quantitative estimation of a solid phase in suspension. It is unsuited to the precise determination of solubility because of the necessity for the presence of a definite quantity of the solid phase in the standard.

Popoff and Neuman⁴ appear to have been the first to utilize an optical method involving the estimation of the solubility of a sparingly soluble inorganic salt by noting the first appearance of the Tyndall beam in a

¹ For suggestion of the problem and for generous assistance in the earlier part of the work the authors are indebted to the late Stephen Popoff.

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³ P. V. Wells, *Chem. Reviews*, **3**, 331-382 (1927).

⁴ Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853-1860 (1930).

series of dilute solutions of suitable reactants under controlled conditions. The present investigation was undertaken for the purpose of establishing the sensitiveness and reliability of such a method and of developing a generalized technique by means of which the solubility of various inorganic precipitates could be measured.

Purification of Materials and Preparation of Solutions

Redistilled Water.—Distilled water from the laboratory supply system was distilled from alkaline potassium permanganate solution in a specially constructed Pyrex glass still provided with a tin condenser tube attached to the still-head by means of a water seal. The Pyrex glass still-head was so constructed as to cause the vapor to reverse the direction of its course twice before entering the condenser, thus eliminating mechanical entrainment of impurities. Dust was excluded by a glass shield which fitted over the neck of the receiver. A portion of each new supply of water was tested in the tyndallmeter with an excess of silver nitrate to insure the absence of dissolved gases of an objectionable nature.

Potassium Chloride.—A good grade of c. p. potassium chloride was twice recrystallized from redistilled water, the hot concentrated solution being filtered through a good grade of filter paper in each case and finally through a glass filtering crucible with sintered glass bottom to remove shreds of filter paper. The recrystallized salt was collected in a similar filtering crucible.

Silver Nitrate.—C. p. silver nitrate, labeled as containing 0.002% of chloride, was used as the starting material. A solution formed by dissolving about 0.01 g. of the solid in a few cubic centimeters of redistilled water showed readily distinguishable opalescence when examined in the tyndallmeter. After two crystallizations from redistilled water a sample of the product yielded a solution which appeared free from opalescence as compared with pure water. The filtering technique was similar to that employed for potassium chloride with the exception that a crucible with sintered glass bottom was used for all filtrations.

Mercurous Perchlorate.—The mercurous perchlorate used in this investigation was prepared by Wirth and Ough as described in the article by them.⁵ The stock solution of this salt was also prepared and analyzed by them as described in the same paper.

Nitric Acid.—C. p. nitric acid was purified by two distillations, rejecting the first and last portions and expelling the oxides of nitrogen, after which it was diluted with redistilled water. It was standardized indirectly against potassium acid phthalate by the use of carbonate-free sodium hydroxide solution.

Perchloric Acid.—70–72% perchloric acid, distilled in vacuum, was diluted with redistilled water and standardized, as in the case of nitric acid, against potassium acid phthalate.

The stock solutions of silver nitrate and of potassium chloride were approximately 0.1 molar. They were prepared by dissolving the moist recrystallized salts in redistilled water. They were analyzed both gravimetrically and by the Mohr titration method using weight burets.

The calculated weight of the stock solution, in the case of each salt, was diluted to two liters in a flask which had been calibrated in terms of a standard (calibrated) 50-cc. pipet. The resulting intermediate solution was diluted, by use of the calibrated pipet and flask, to a concentration of 2.608×10^{-4} mole of salt per liter to form the experimental solutions. Equal volumes of the experimental solutions of the two salts were stoichiometrically equivalent. Assuming a value of 1.304×10^{-4} mole per liter for the

⁵ Popoff, Riddick, Wirth and Ough, *THIS JOURNAL*, **53**, 1195 (1931).

solubility of silver chloride, a mixture containing 5 cc. of each of the experimental solutions in sufficient water to make a total volume of 100 cc. should just initiate precipitation of silver chloride at a temperature of 25°.

The concentration of the experimental solution of potassium chloride used for determining the solubility of mercurous chloride was 2×10^{-4} mole per liter. That of the mercurous perchlorate solution was 1×10^{-4} mole per liter. Assuming the solubility of mercurous chloride to be 5×10^{-6} mole per liter, a condition of incipient precipitation should be reached by mixing together 5 cc. of each of the experimental solutions with water in a total volume of 100 cc. at a temperature of 25°.

Optical Instruments and Accessories.—The tyndallmeter used in this investigation, and previously used by Popoff and Neuman,⁶ is a modified form of the instrument used by Tolman and co-workers.⁷

A brass bottle-holder, blackened inside to eliminate reflection and provided with suitable openings, was designed and used by the authors.

The Gradation Photometer, or "Stupho," as originated by C. Pulfrich and manufactured by Carl Zeiss, Incorporated, was used in conjunction with the tyndallmeter.

Great difficulty was experienced in finding suitable containers for the suspensions; 100-cc. oil sample bottles of moulded glass, although fairly satisfactory in other respects, invariably caused contamination of the contents when agitated in the bath. Protection by application to the corks of melted paraffin, both externally and internally, failed to eliminate this difficulty. In fact, pieces of clean paraffin agitated with pure water for a period of an hour or more always caused turbidity, possibly due to the formation of an emulsion. Rubber stoppers, cleaned by the usual laboratory methods, were even less satisfactory. A minute quantity of foreign solid material, the presence of which might not adversely affect other methods, renders photometric measurements unreliable.

Cylindrical flat-bottomed bottles with rounded shoulders were fashioned to dimensions of about 3.2×20 cm. from heavy-walled moulded Pyrex tubes. The neck of a bottle was formed by sealing a piece of Pyrex tubing of 12 mm. diameter to the rounded shoulder. The volume of each bottle was about 125 cc., allowing sufficient free space to provide for thorough mixing of the contents when the bottles were laid in the bath and rocked about a horizontal axis perpendicular to the length of the bottle.

Experimental Method

The method of determining the solubility of a substance consisted essentially of the examination in the tyndallmeter and in the gradation photometer of a series of sealed bottles containing mixtures of extremely dilute solutions of the reactants in water or in dilute acid. Equal volumes of the experimental solutions were always used. By successively increasing the amounts of the two reactants in a total volume of 100 cc., turbidity was caused in the more concentrated of a series of such solutions. The value for the solubility of the saturating phase was considered to be between the highest concentration which failed to show turbidity and the lowest concentration at which turbidity could be seen when the bottles were examined in the optical instruments.

To avoid the formation and consequent partial settling of a true precipitate, the solutions were added to the bottle in the following order:

⁶ Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853-1860 (1930).

⁷ Tolman and Vliet, *THIS JOURNAL*, **41**, 297 (1919).

one of the reactants, nearly all of the water (or the dilute acid if an acid was used), the other reactant, and finally the remainder of the water required to give a total volume of 100 cc.

After the bottles had been sealed in a blast lamp they were immersed in a constant temperature water-bath, maintained at a temperature of $25 \pm 0.02^\circ$, in which they were agitated for a period of at least four hours. Results of tests covering periods of time up to seventy-two hours indicated no significant change between four and twenty-four hours in the case of barely perceptible turbidities. Longer periods of time caused opalescence and settling of the suspended particles in even the most dilute suspensions.

An attempt was made to approach equilibrium from both lower and higher temperatures. Cooling about 0.2° for one hour with subsequent shaking for four hours or longer at 25° produced no perceptible change in the results. Cooling in ice water for half an hour caused opalescence and settling of suspended particles. A suspension could not again be obtained after this treatment.

After the bottles were removed from the bath they were carefully wiped clean and dry before being placed in the optical instruments. The importance of having the bottles clean cannot be too strongly emphasized. Before immersion in the reservoir of the gradation photometer the bottles were rinsed with distilled water at room temperature to remove particles of lint or dust. The distilled water in the reservoir was changed frequently. The entrance of dust or other foreign material was carefully guarded against. Readings were made in a darkened room only after the eye of the observer had become accustomed to the subdued light

Experimental Results and Discussion

TABLE I
SILVER CHLORIDE

Molarity of HNO_3	$S \times 10^5$ of AgCl		Molarity of HNO_3	$S \times 10^5$ of AgCl	
0.0000	1.49	1.56	0.119	1.62	
.0024	1.41	1.45	.238	1.70	
.0238	1.51	1.56	.524	2.35	2.40

TABLE II
MERCUROUS CHLORIDE

Molarity of HClO_4	$S \times 10^5$ of Hg_2Cl_2	Molarity of HNO_3	$S \times 10^5$ of Hg_2Cl_2
0.0005	4.7	0.005	5.2
.005	4.8	.010	5.6
.010	5.0	.100	5.8
.100	5.5		
.200	6.3		

The S in Tables I and II represents the solubility in moles per liter of the saturating phase at a temperature of 25° .

The value for the solubility of silver chloride in water at 25°, as recorded in the "International Critical Tables,"⁸ is 1.304×10^{-5} mole per liter. Pinkus and Berkolaiko,⁹ using a method in which the final measurement of solubility was made with the aid of a nephelometer, found 1.42×10^{-5} . Popoff and Neuman,⁴ also using an optical method, reported 1.278×10^{-5} .

Our values are somewhat higher than those obtained by others. The possibility of the existence of supersaturation was considered and precautions were taken to eliminate it. Solutions cooled to incipient turbidity and subsequently agitated at 25° for several hours failed to show any evidence of the presence of precipitated material in any concentration less than that originally required to show turbidity. Although a suspension could not again be obtained after this treatment, the presence of precipitated material could be easily detected in the more concentrated solutions by vigorously shaking the bottles, allowing them to stand undisturbed for one minute to allow entrapped air bubbles to escape, and then examining them in the tyndallmeter.

As indicated in Table I, the solubility of silver chloride evidently reaches a minimum in the presence of a very small quantity of nitric acid rather than in water containing only silver chloride and the exceedingly small quantity of potassium and nitrate ions from the reactants. The danger of error involved in extrapolation to zero concentration of a solvent electrolyte is thus strikingly shown.

Previous to 1904 the published values of the solubility of mercurous chloride varied from 1×10^{-6} to 6×10^{-6} mole per liter. Ley and Heimbucher,¹⁰ using an electromotive force method, found 0.8×10^{-6} . Brodskii,¹¹ also using an electromotive force method, reported 1.15×10^{-18} as the solubility product of mercurous chloride at 25° which would indicate a solubility of the order of 6.6×10^{-7} .

The sensitiveness of our method was ascertained by determining the smallest amounts of the reactants by which a non-turbid solution could be made to show turbidity. The amount of silver chloride required to produce a perceptible change was approximately 5×10^{-7} mole per liter. The sensitiveness has therefore been stated as $\approx 2.5 \times 10^{-7}$ mole per liter. Likewise, the sensitiveness in the case of mercurous chloride is approximately $\approx 1 \times 10^{-7}$ mole per liter.

The precision attainable in photometric measurements is commonly assumed to be of the order of 0.5 to 0.2% under the most favorable conditions. The term "favorable conditions" includes uniformity of particle size in the suspended medium. Until the difficulty of obtaining even approximate uniformity of particle size by precipitation

⁸ "International Critical Tables," 1929, Vol. VI, p. 256.

⁹ Pinkus and Berkolaiko, *J. chim. phys.*, **27**, 364-385 (1930).

¹⁰ Ley and Heimbucher, *Z. Elektrochem.*, **10**, 301-3 (1904).

¹¹ Brodskii, *ibid.*, **35**, 833 (1929).

methods can be at least minimized, it is probable that the photometric method cannot be made sufficiently sensitive to replace older methods of determining solubility. The present investigation has demonstrated, however, that experimental data secured by photometric measurements may serve as a valuable check on the accuracy of other methods. Obviously it cannot be used for very soluble substances, and probably not for extremely insoluble ones such as copper sulfide.

The experimental work is tedious. It is extremely difficult, under ordinary working conditions, to exclude completely dust and traces of stopcock grease from the solutions while they are being transferred, and to prevent contamination by traces of hydrogen chloride, ammonia and other undesirable gases from adjacent laboratories. In view of these and other limitations the method cannot be said to be of general applicability in its present stage of development.

Some interesting observations were made during attempts to stabilize suspensions of inorganic salts by means of protective colloids. The results are not included here because of the uncertainties involved in any interpretation of solubility data obtained in the presence of a stabilizing agent.

The junior author was indebted to Associate Professor Stephen Popoff, Head of the Analytical Division, Department of Chemistry and Chemical Engineering, State University of Iowa, for suggesting the problem in photometry and for his assistance in the earlier part of the work. The authors, however, assume responsibility for this report, the major portion of which is based on research done after Dr. Popoff was obliged because of prolonged illness to relinquish supervision of the work.

Summary

1. An improved technique for the photometric determination of the solubility of sparingly soluble salts has been developed, employing a modified tyndallmeter and a gradation photometer to detect the appearance of turbidity in the solutions.

2. The solubility of silver chloride in five concentrations of nitric acid and in water containing potassium and nitrate ions from the reactants which produced the silver chloride was measured at 25°. The solubility in water was found to be between 1.49 and 1.56×10^{-5} mole per liter. The solubility was found to vary from 1.43×10^{-5} in 0.0024 molar nitric acid to 2.37×10^{-5} in 0.524 molar nitric acid.

3. The solubility of mercurous chloride in five concentrations of perchloric acid and in three concentrations of nitric acid was measured at 25°. It was found to vary from 4.7×10^{-6} mole per liter in 0.0005 molar perchloric acid to 6.3×10^{-6} in 0.200 molar perchloric acid; and from 5.2×10^{-6} in 0.005 molar nitric acid to 5.8×10^{-6} in 0.100 molar nitric acid.

4. The sensitiveness of the method is of the order of $\approx 2.5 \times 10^{-7}$ mole per liter for silver chloride in nitric acid of concentrations from 0.0024 to 0.240 *M*. In the case of mercurous chloride the sensitiveness is of the order of $\approx 1 \times 10^{-7}$ mole per liter.