Summary

1. The equilibrium constants for the reactions between H_2O, HDO, D_2O, C_2H_2, C_2HD and C_2D_2 have been determined experimentally at 0 and 100°.

2. From a knowledge of the change of the equilibrium constants of isotopic exchange reactions with the temperature (in the range 0 to 100°), the heats of reaction of these exchanges have been calculated.

MINNEAPOLIS, MINN. RECEIVED FEBRUARY 19, 1937

[CONTRIBUTION FROM THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

A Polarimetric Method for the Determination of Water in Acetic Acid[1]

BY GERRIT TOENNIES AND MARGARET ELLIOTT

Some recently proposed methods for the determination of water in organic media are based on the acidimetric determination of acetic acid formed from acetyl chloride[2] or from acetic anhydride.[3] Application of these methods to the determination of water in acetic acid or similar liquids, although possible in principle, is obviously limited in accuracy and sensitivity by the large acidimetric blank value of the acetic acid. This limitation would be abolished if in the method of Toennies and Elliott[3] the acetic anhydride could be replaced by an optically active anhydride the hydration of which is measurable by an accompanying change in optical rotation. *d*-Camphoric acid and the corresponding anhydride differ widely in their effect on polarized light, but the hydration of camphoric anhydride

$$C_8H_{14}(CO)_2O + H_2O \longrightarrow C_8H_{14}(COOH)_2 \quad (1)$$

in acetic acid solution, although susceptible to acid catalysis,[4] was found to be too slow, with tolerably low acid concentrations (in presence of 0.1 *M* $HClO_4$ $k_{25} \cong 10^{-3}$), to be of practical promise. On the other hand, the complete absence of a conceivable[5] interfering reaction

$$C_8H_{14}(CO)_2O + 2CH_3COOH \longrightarrow C_8H_{14}(COOH)_2 + (CH_3CO)_2O \quad (2)$$

—in spite of the large excess of one of the potential reactants (CH_3COOH)—suggested the probability of a strong thermodynamic tendency for the opposite of reaction (2)

$$(CH_3CO)_2O + C_8H_{14}(COOH)_2 \longrightarrow 2CH_3COOH + C_8H_{14}(CO)_2O \quad (3)$$

This was found to exist: the bimolecular constant[6] of this reaction in acetic acid is directly proportional to the amount of strong acid present[7] and is, in the presence of 0.001 *M* perchloric acid and at about 25°, of the order of 10^{-1}; *i. e.*, with equal amounts of catalyst, reaction (3) is estimated to be 10^4 times as fast as reaction (1). Therefore, and since the acid-catalyzed reaction of acetic anhydride with moderate amounts of water in acetic acid is even more rapid than reaction (3), the following principle for the determination of water in glacial acetic acid suggests itself.

In the presence of a suitable small concentration of a strong acid (perchloric acid) the acetic acid solution of water is allowed to react with a measured quantity of acetic anhydride, and the unused amount of acetic anhydride is determined by the decrease in optical rotation coincident with its reaction with a measured amount of *d*-camphoric acid.

The experimental investigation of the method has been confined to a demonstration of its practicability and its minimum accuracy, while it has not been extended either to a quantitative study of various factors that might add to its refinement (such as temperature, concentration or mutual effects on the specific rotations of *d*-camphoric acid and *d*-camphoric anhydride) nor to a consideration of possible interfering substances (such as might conceivably be formic acid or

---

[1] Aided by the Robert McNeil Fellowship maintained by McNeil Laboratories, Inc.

[2] D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **57**, 841 (1935).

[3] G. Toennies and M. Elliott, *ibid.*, **57**, 2136 (1935).

[4] The catalysis of the hydration of organic anhydrides by strong acids in non-aqueous media, first suggested by observations of Orton and Jones [*J. Chem. Soc.*, **101**, 1708 (1912)] on acetic anhydride and confirmed by observations made in this Laboratory [Toennies and Lavine, *J. Biol. Chem.*, **100**, 474 (1933); Lavine and Toennies, *ibid.*, **101**, 732 (1933); ref. 3], has been studied by us on a number of anhydrides of different types, and widely differing rates of catalysis have been found (results to be published).

[5] The analogous reaction $(C_6H_5CO)_2O + 2CH_3COOH \longrightarrow 2C_6H_5COOH + (CH_3CO)_2O$ has been described: R. Kremann and W. Rösler, *Monatsh.*, **43**, 358 (1925); *C. A.*, **17**, 1426 (1923).

[6] All velocity constants are expressed in moles per liter per minute.

[7] G. Toennies and M. Elliott, abstracts of papers to be presented before the Division of Physical and Inorganic Chemistry at the Meeting of the American Chemical Society, Chapel Hill, N. C., April, 1937.

acetone[3]), nor to an exploration of its applicability to other acid or non-acid media.

Experimental

Reagents: Perchloric Acid Solution.—By dissolving a weighed amount of standardized concentrated perchloric acid in acetic acid[8] a solution of 1.00 *M* perchloric acid and 2.70 *M* water (exclusive of the water content of the acetic acid) was prepared. Repeated titration with an acetic acid solution of piperidine, with crystal violet as the indicator,[9] showed complete stability.

Acetic Anhydride.—The percentage of acetic anhydride (x) in a concentrated preparation was calculated from the average equivalent weight (e. w.) obtained by methylate titration[10,3] of a suitable aliquot dissolved in acetonitrile

$$\frac{x}{102.05} + \frac{100 - x}{60.03} = \frac{100}{\text{e. w.}}$$

The preparation used (Merck Reagent) showed 95.4 ± 0.2% acetic anhydride.

***d*-Camphoric Acid and *d*-Camphoric Anhydride.**—The camphoric acid used (Eastman) had a melting point of 187.5°, corr. (Beilstein 187°, corr.), and an equivalent weight, by methylate titration,[10,3] of 100.1 (calcd. 100.1). Determinations of the specific rotation[11] in acetic acid gave $[\alpha]_{\mathrm{Hg}}^{27\pm1}$ + 53.9 ± 0.1° in 0.25 *M* solution, and $[\alpha]_{\mathrm{Hg}}^{27\pm1}$ +54.25 ± 0.1° in 0.05 *M* solution, while *d*-camphoric anhydride in 0.25 *M* solution showed $[\alpha]_{\mathrm{Hg}}$ −0.8 ± 0.2°. Ten cc. of acetic acid was found to dissolve at room temperature more than 0.5 but less than 0.6 g. of *d*-camphoric anhydride.

Reaction Velocities.—The velocity of the acid-catalyzed reaction between camphoric anhydride and water is illustrated by the experiment recorded in Table I. The bimolecular constant, calculated over the range of 25 to 89% conversion of the anhydride, shows a uniformly increasing trend which tends to disappear when it is assumed that the velocity is inversely proportional to the water content of the medium (Table I, column 4). This assumption may be justified as an approximation in view of the fact that H_2O, due to its basic properties in acetic acid,[12,9] will lower the acid potential of the catalyst

$$\mathrm{HClO_4} \begin{cases} +\mathrm{CH_3COOH} \rightleftarrows \mathrm{CH_3COOH_2^+} + \mathrm{ClO_4^-} \\ +\mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{ClO_4^-} \end{cases}$$

In another experiment with initial concentrations in acetic acid, of 0.334 *M* H_2O, 0.550 *M* $(CH_3CO)_2O$, 0.219 *M* $C_8H_{14}(CO)_2O$ and 0.10 *M* $HClO_4$, the rotation (2-dm. tube, α_{Hg}) remained −0.03 ± 0.02° over a period of ten days, indicating that the water had reacted completely with the acetic anhydride and that reaction (2) does not take place. This, in conjunction with the following experiments showing the ease and completeness of the opposite reaction (3), seems sufficient evidence for the conclusion that under the experimental conditions a reaction between camphoric anhydride and acetic acid is thermodynamically impossible.

TABLE I

REACTION BETWEEN *d*-CAMPHORIC ANHYDRIDE AND WATER

Initial concentration of camphoric anhydride, b = 0.270 *M*; of water, estimated from water content of acetic acid, as determined (*v. infr.*), and from water introduced by 0.25 cc. of 10.9 *M* $HClO_4$, a = 0.362 *M*. Medium: acetic acid. Catalyst: 0.11 *M* $HClO_4$. Temperature: 24.0 ± 1.5°. $\alpha = \alpha_{\mathrm{Hg}}$ measured in a 2-dm. tube. The values of the third column have been obtained by integrations over the successive intervals of time, and those of the fourth column by multiplying each value of the third with the mean value of the water concentration for each interval. In a control tube, without catalyst, (b = 0.273 *M*, a = 0.068 *M*) the rotation remained, over a period of seven days, α = −0.07 ± 0.02°.

Hours	α	$k \times 10^3$	$k(a - x) \times 10^3$
19.5	+1.41	0.75	2.47
43.5	+2.92	1.13	2.96
67.5	+3.99	1.59	3.21
90.0	+4.71	2.29	3.68
115.5	+5.20	2.73	3.63

The velocity of the reaction between camphoric acid and acetic anhydride (3) was investigated in the following experiments. A solution of the initial concentrations 0.067 *M* H_2O, 0.688 *M* $(CH_3CO)_2O$, 0.216 *M* $C_8H_{14}(COOH)_2$ and 0.001 *M* $HClO_4$ showed in the 2-dm. tube the following rotations:

Minutes	7	10	12	14
α_{Hg}	2.73°	2.22°	1.91°	1.60°
Minutes	16	20	25	32
α_{Hg}	1.40°	0.90°	0.60°	0.32°

The temperature was 25–26°. Calculation of the bimolecular constants for the points of 20, 40, 60 and 80% conversion of the camphoric acid, obtained from the plotted curve and from the calculated initial and final rotations +4.67 and −0.06°, gives k = 0.135 ± 0.007, the assumption being made that the water present is eliminated at once by reacting with the equivalent amount of acetic anhydride. A similar solution containing 0.01 *M* perchloric acid showed after ten minutes the calculated value for camphoric anhydride. In the presence of 0.0001 *M* perchloric acid, on the other hand, the same reaction was 50% complete after twenty-five hours, while in the absence of any added catalyst a corresponding half time of ninety hours was found. No quantitative conclusions should be drawn from the latter two data, as without special precautions interference by contamination with minute amounts of either acid or basic material must be considered possible. However, on the basis of these experiments 1 to 5 × 10^{-3} *M* perchloric acid was selected as a catalytic agent suitable to ensure sufficiently rapid completion of the reaction of camphoric acid with acetic anhydride in the presence of an adequate excess of the latter.

Determination of Water Present in Glacial Acetic Acid.—The first experiment was based on the tentative assumption that the water content of the glacial acetic acid at hand ("assay 99.5% CH_3COOH") would be be-

---

[8] Glacial Acetic Acid "Merck Reagent" was used throughout this work.

[9] J. B. Conant and T. H. Werner, THIS JOURNAL, **52**, 4436 (1930).

[10] T. F. Lavine and G. Toennies, *J. Biol. Chem.*, **101**, 727 (1933).

[11] For the polarimeter and light source used *cf. J. Biol. Chem.*, **89**, 155 (1930).

[12] N. F. Hall and J. B. Conant, THIS JOURNAL, **49**, 3055 (1927).

tween 0.3 and 0.7% (0.16–0.40 M water). An acetic acid solution containing 8.822 g. of 95.4% acetic anhydride (=8.5 cc.) per 100 cc. was used. To 6.44 mml. of camphoric acid in a 25-cc. flask 12.5 cc. of the acetic anhydride solution (10.31 mml. $(CH_3CO)_2O$) and 1.25 cc. of 0.1 M perchloric acid in acetic acid (=0.125 mml. $HClO_4$ with 0.34 mml. H_2O) were added, and the solution was completed to 25 cc. with acetic acid. The contribution of camphoric acid to the total volume under the conditions of these experiments was determined as approximately 0.845 cc. per gram. Accordingly the amount of acetic acid present is, with sufficient accuracy, 25.00 − 1.06 (acetic anhydride) − 1.09 (camphoric acid) = 22.85 cc. This solution showed after one hour a constant rotation of $\alpha_{Hg} = -0.08°$ (2-dm. tube), indicating complete conversion of camphoric acid into the anhydride. If the assumption is correct that acetic anhydride reacts much more rapidly with water than with camphoric acid this result shows that the acetic acid cannot have contained more than 10.31 (= total $(CH_3CO)_2O$) − 6.44 (= $C_8H_{14}(COOH)_2$) − 0.34 (= H_2O introduced with $HClO_4$) = 3.53 mml. H_2O, *i. e.*, the water content was less than 3.53/22.85 = 0.154 M (0.278 g. per 100 cc.).

Accordingly the following two solutions were made, using the same stock solutions as in the preceding experiment: (A) 6.45 mml. $C_8H_{14}(COOH)_2$, 4.12 mml. $(CH_3CO)_2O$ and 0.12 mml. $HClO_4$ + 0.33 mml. H_2O and (B) 6.50 mml. $C_8H_{14}(COOH)_2$, 6.60 mml. $(CH_3CO)_2O$ and 0.125 mml. $HClO_4$ + 0.34 mml. H_2O, both completed to 25 cc. with acetic acid. After two hours the rotation (α_{Hg}, 2 dm.) was found to be stationary in both solutions, solution (A) showing +3.71 ± 0.005° and (B), +1.565 ± 0.015°. These values correspond to 33.0 and 71.2% conversion of camphoric acid into anhydride (obtained by using the values of +54.0 and −0.8° for the specific rotations of the two forms); *i. e.*, 2.13 and 4.63 mml. camphoric acid, respectively, have reacted with an equivalent amount of acetic anhydride. This leaves 4.12 − 2.13 = 1.99 and 6.60 − 4.63 = 1.97 mml. of acetic anhydride which must have reacted with equivalent amounts of water. 0.33 and 0.34 mml., respectively, are accounted for by the water introduced with the perchloric acid, leaving 1.66 and 1.63 mml. of water, which must have been present in the acetic acid. The amounts of the latter used were 25.00 − 1.09 (volume of camphoric acid) − 0.43 (volume of acetic anhydride) = 23.48 cc. and similarly 25.00 − 1.10 − 0.68 = 23.22 cc. so that 1.66/23.48 = 0.0707 M and 1.63/23.22 = 0.0702 M are the values obtained in two separate experiments for the water concentration, equal to 0.127 ± 0.0005% by volume.

Although the close agreement between the results of two determinations—in which the amounts (relative and absolute) of acetic anhydride used differed in the ratio of 5:8—seemed sufficient evidence for the validity of the method, this was verified by a set of determinations in which a known amount of water was added to the acetic acid. An additional purpose of this experiment was to see whether the time allowed for the reaction between acetic anhydride and water previous to the addition of camphoric acid could have any influence on the result, or, stated differently, if in the competition between camphoric acid and water for acetic anhydride the latter could be used up before all of the water had reacted. If this were possible the remaining water would react extremely slowly with camphoric anhydride (*cf.* under Reaction Velocities). 15.00 cc. of an acetic acid solution containing 52.16 mml. of $(CH_3CO)_2O$ (= 5.14 cc. 95.4% acetic anhydride), 0.520 cc. of H_2O (= 28.9 mml.) and 0.10 mml. of $HClO_4$ together with 0.27 mml. of H_2O were made up to approximately 100 cc. with acetic acid. The solution weighed 104.62 g. and contained the following amounts of water.

(100.00 − 5.14 − 0.52) 0.0705	= 6.65 mml.	(water content of the acetic acid, based on the preceding determination)
0.520/0.018	= 28.86 mml.	(added water)
	0.27 mml.	(introduced with $HClO_4$)
	35.78 mml.	

or 0.3420 mml. of H_2O per gram of solution.

25-cc. flasks, containing weighed amounts of camphoric acid, were filled to volume with the described solution, the exact amount of solution used being determined by weighing. Table II summarizes the results of this experiment.

TABLE II

DETERMINATION OF A KNOWN AMOUNT OF WATER IN ACETIC ACID SOLUTION

This table should be read in the light of the preceding text. The following notes, referring to the horizontal columns, will assist in its interpretation: $d = \frac{c \times 52.16}{104.62}$, $g = \frac{54.0 \times 2 \times e \times 0.2001}{f}$, $i = \frac{(g - h)100}{g + 0.075}$, $k = \frac{e \times i}{100}$, $l = d - k$, $m = l/c$.

(a)	Time between adding catalyst to the acetic anhydride-acetic acid–water mixture and combining the resulting solution (b) with camphoric acid, min.	6	12	120
(c)	Amount of solution (b) used, g.	24.97	24.79	24.95
(d)	Amount of acetic anhydride present, mml.	12.45	12.36	12.44
(e)	Amount of camphoric acid, mml.	6.50	6.72	6.49
(f)	Volume, cc.	25.05	25.00	25.10
(g)	Calculated initial rotation (2-dm. tube), α_{Hg}	5.61°	5.805°	5.59°
(h)	Final rotation, determined after 4 and 20 hours, α^{27}_{Hg}	2.265°	2.50°	2.285°
(i)	Fraction of camphoric acid converted into anhydride, according to (h), %	58.8	56.2	58.3
(k)	Acetic anhydride consumed by reaction with camphoric acid, mml.	3.815	3.775	3.78
(l)	Acetic anhydride consumed by reaction with water, mml.	8.635	8.585	8.66
(m)	Water initially present, per gram of solution (b), mml.	0.346	0.346	0.347

The amount of water found lies within approximately 1% of the calculated value and appears independent of the time allowed for the separate reaction between acetic anhydride and water, indicating that this reaction is much faster than the one between acetic anhydride and camphoric acid. This is in agreement with the data of Orton and Jones (*cf.* footnote 4) and is also evident from the observation, in this last experiment, of a considerable evolution of heat as soon as the catalyst was added even though its concentration was only 0.001 *M*.

Outline of a Practical Method.—The specific rotation of *d*-camphoric acid to be used is determined in about 0.25 *M* solution in glacial acetic acid. About 6.5 mml. of *d*-camphoric acid is weighed accurately in a 25-cc. volumetric flask, a definite amount of standardized acetic anhydride—the amount to be used is chosen so that after reaction with the expected amount of water 3.25 ± 3 mml. of $(CH_3CO)_2O$ remain for reaction with camphoric acid—is added and the flask is filled up to the mark with the acetic acid to be tested, including in the total volume 0.125 mml. of perchloric acid of known water content (*e. g.*, 0.125 cc. of a 1.00 *M* $HClO_4$ solution in acetic acid made from 70.0% aqueous perchloric acid would contain 0.299 mml. of H_2O). The amount of acetic acid employed is obtained by deducting the known volumes of the other ingredients from the total volume, using 0.845 as the partial specific volume of *d*-camphoric acid or, more accurately, by weighing. From the resulting solution a 2-dm. polarimeter tube is filled and polarimetric readings are taken until the optical rotation has become stationary. If the stationary value corresponds to the specific rotation of *d*-camphoric acid or to that of *d*-camphoric anhydride ($[\alpha]_{Hg} = -0.8°$) a new experiment with a larger or smaller amount, respectively, of acetic anhydride is started. The difference between the initial amount of acetic anhydride and the polarimetrically determined amount of camphoric anhydride formed is equivalent to the amount of water present. For confirmation of the result the determination should be repeated with a different amount of acetic anhydride.

Discussion

The amount of water present per gram of solution, expressed in the terms used in Table II, is

$$m = \frac{d}{c} - \frac{e(2 \times 0.2001 \times [\alpha]_1 \times e - fh)}{c(2 \times 0.2001 \times [\alpha]_1 \times e + 2 \times 0.1821 \times [\alpha]_2 \times e)}$$

where $[\alpha]_1$ and $[\alpha]_2$ are the specific rotations of camphoric acid and camphoric anhydride, respectively. By means of the probability theorems relating to the probable errors of arithmetically combined measurements,[13] the probable error of *m* may be calculated in algebraic terms. On the basis of the analytical experience of the present study the following estimated probable errors may be tentatively assigned:

Amount of acetic anhydride	d/c	±0.2%
Specific rotation of camphoric acid	$[\alpha]_1$	±0.3%
Specific rotation of camphoric anhydride	$[\alpha]_2$	±15%
Final rotation	h	±0.4%
Amount of camphoric acid	e/c	±0.2%

Application of these probable errors to the data results in a probable error, for the *single* determination, of ±1.8% in the most unfavorable case of determination *B* (p. 904 and of ±0.5% for each single determination of Table II. These computations, together with the actual results, point to a precision and probable accuracy of the method of at least ±1% for water concentrations of 0.1 to 1%. Undoubtedly this figure could be appreciably improved by more refined measurements.

A comparison of the analytical results with those obtainable by other methods has not been attempted as the limitations of available methods seemed to preclude the possibility of yielding results of comparable accuracy. Since the literature values[14] for the absolute freezing point of acetic acid vary at least between 16.62 and 16.67° an attempt to determine the freezing point of the acid used in the present work with an accuracy of 0.002°, corresponding to a variation in the water content of 0.001%, would appear futile. An alternative physical method based on critical solution temperatures,[15] although of about six times higher temperature sensitivity than the freezing point method, is also limited by the lack of absolute standard data. The chemical method of K. Fischer,[16] which is based on the fact that iodine is reduced by sulfur dioxide only in the presence of water, and which in regard to sensitivity is comparable with the present method, has not been applied by its author to acetic acid and may not be applicable without considerable additional research.

Summary

The amount of water present in acetic acid can be determined by allowing it to react with a known amount of acetic anhydride and by determining the excess of acetic anhydride by the decrease in optical rotation caused by its reaction with *d*-camphoric acid, by which the latter is converted into *d*-camphoric anhydride. Both reactions involved are strongly catalyzed by low concentrations of strong acids. The accuracy

---

(13) *Cf. e. g.*, J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green & Co., New York, 1929, pp. 527-530.

(14) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Third Supplement, Verlag von Julius Springer, Berlin, 1936.

(15) D. C. Jones, *J. Chem. Soc.*, **123**, 1374 (1923).

(16) K. Fischer, *Z. angew. Chem.*, **48**, 394 (1935).

of the method is characterized by determinations of 0.1 and 0.6% of water, within limits of ±0.001 and ±0.008% respectively.

PHILADELPHIA, PENNA. RECEIVED JANUARY 16, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Chemical and X-ray Investigation of Barium Sulfate Contaminated with Permanganic Acid[1]

BY PHILIP R. AVERELL AND GEORGE H. WALDEN, JR.

Introduction

A recent article by Walden and Cohen[2] reported the results of an investigation of barium sulfate precipitates contaminated with nitrate. The results of this work indicated the necessity of a similar investigation using a contaminating ion of different configuration, such as permanganate ion. Several investigators, notably Grimm and Wagner[3] have reported on the precipitation of barium sulfate in the presence of potassium permanganate.

The present investigation deals with (1) the precipitation of barium sulfate in the presence of permanganate ion, hydrogen ion being the only other foreign ion present; (2) the establishment, by chemical analysis, of the complete constitution of these contaminated precipitates, thereby identifying the cation which balances the charge of the coprecipitated permanganate ion; (3) investigation of the character of the precipitates by means of X-ray powder photographs.

It developed that the method of precipitation used by Walden and Cohen,[2] which for them produced beautifully coarse crystalline precipitates contaminated with nitrate ion, yielded for us precipitates so fine as to appear amorphous even when examined between crossed nicols under an oil-immersion objective, and which gave only a vague trace of an X-ray diffraction pattern. The method of precipitation used by Grimm and Wagner,[3b] adapted to the new conditions, proved to be apparently the only one which would yield precipitates of the desired coarseness.

Complete analyses of samples prepared by both methods showed that barium and sulfate ions exist in the precipitates always in a mole ratio of 1:1, which shows that the ion accompanying the permanganate ion is not barium, and therefore must be hydrogen or a hydrated hydrogen ion.

X-ray powder photographs showed a definite and fairly regular expansion of the lattice parameters with increased contamination, a conclusive evidence of the existence of solid solution.

Method of Preparation.—The method of precipitation used by Walden and Cohen, adapted to the study of permanganate contamination, consists of the slow addition of a sulfuric–permanganic acid solution to a barium permanganate–permanganic acid solution, the concentrations being so adjusted that the permanganate concentration is the same in both solutions; the sulfuric acid added is sufficient to precipitate less than half of the barium ion. The method of Grimm and Wagner, adapted to the present investigation, is to mix rapidly two solutions containing respectively equimolar quantities of barium permanganate and sulfuric acid. Each solution contains in addition permanganic acid in such amount that the permanganate ion concentrations are equal.

Since the unpreventable spontaneous decomposition of permanganic acid made it impossible to keep the system free of manganese dioxide, it was necessary to use all solutions as quickly after preparation as possible, and to use some means of removing manganese dioxide from the precipitate before final filtration, washing and drying. Accordingly, after the mother liquor was removed, the precipitate was given one washing with either sulfur dioxide solution or dilute hydrogen peroxide acidified slightly with hydrochloric acid, followed by water. All washings were made more effective by centrifugal drainage. As the slow drying of water-wet precipitates also caused decomposition with formation of manganese dioxide, this difficulty was obviated—again using Grimm's procedure—by washing with acetone four or five times, the last washings being colorless, then with anhydrous ether, before drying in air or over concentrated sulfuric acid.

The product thus prepared is a beautiful rose-colored precipitate, showing no traces of manganese dioxide, either to the unaided eye or under a microscope. As in the case of the precipitates described by Grimm, the co-precipitated permanganate ion is chemically very inert. The color is not noticeably bleached by contact with strong reducing solutions even after standing for several days. Heating at 110° for twenty to forty hours produces decomposition only in insufficiently washed precipitates, and in

---

[1] Dissertation submitted by Philip R. Averell in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. The material was presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] Walden and Cohen, THIS JOURNAL, **57**, 2591 (1935).

[3] (a) Grimm, *Z. Elektrochem.*, **30**, 467 (1924); (b) Grimm and Wagner, *Z. physik. Chem.*, **132**, 131 (1928); (c) Wagner, *ibid.*, **2B**, 27 (1929).