tion. The electronic polarization P_E was obtained from the molar refraction at infinite wave length, 27.9 ml. Assuming P_A to be 10% of P_E, the dipole moment of 2-picoline is calculated to be 1.92 *D* with a probable accuracy of ±0.01°. This value is not in good agreement with that of 1.72 *D* (the only previously reported work) obtained by Rau and Narayanaswany[7] because these workers employing the temperature solution method obtained a falsely high value, 23.2 ml. for P_A.[17] The value obtained by Rau and Narayanaswany for the total polarization at infinite dilution $P^{30}_{2\infty}$ is 111.36 ml., in fair agreement with the value obtained here.

Absorption Spectra.—In Figs. 1 and 2 are presented the infrared and ultraviolet absorption curves, respectively, for 2-picoline. The main infrared absorption maxima are presented in Table IV. The main ultraviolet absorption maxima are located at 252, 256.5, 262, and 268 millimicrons. The data were kindly determined by the Koppers Spectrographical Research Laboratory under the direction of Dr. J. J. McGovern.

TABLE IV

MAIN INFRARED ABSORPTION MAXIMA OF 2-PICOLINE

λ in μ	I^a	λ in μ	I^a
1.70	w	7.74	m
2.20	w	8.09	m
2.34	w	8.70	m
2.47	w	9.09	m
2.93	w	9.53	m-i
3.33	m	10.03	m-i
3.66	w	10.24	m
3.82	w	10.65	w
6.29	m-i	11.29	w
6.80	m-i	12.55	w
6.99	m	13.28	i
7.28	w	13.69	m

[a] Approximate intensity: w = weak, m = moderate, i = intense.

Summary

1. 2-Picoline has been purified by fractional distillation and recrystallization to an estimated 99.85 mole % purity.

2. The following properties have been determined for the purified material: freezing point, boiling point, density at 10° intervals from 20 to 80°, the expansion coefficients in the same temperature range, the viscosity at 10° intervals from 0 to 80°, refractive indices at 20 and 30° at 5893, 5461 and 4358 Å., the dipole moment, and the infrared and ultraviolet absorption spectra.

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(17) "The temperature solution method gives only the dipole moment qualitatively and seriously misleads investigators regarding the magnitude of the atomic polarization," H. O. Jenkins, *Trans. Faraday Soc.*, **30**, 741 (1934).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMICAL ENGINEERING AND OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Density of Aqueous Hydrogen Peroxide Solutions[1]

BY CHARLES E. HUCKABA AND FREDERICK G. KEYES

Introduction

A relatively small amount of exact density data exists for aqueous solutions of hydrogen peroxide, due to the decomposition caused by the catalytic activity of glass surfaces which introduces error in the density determination because of combined gas formation and loss of peroxide. A solution of this major problem was found in the preconstruction treatment of the interior surface of the glass from which the vessels were blown, combined with the employment of certain precautions during their use.

The literature reveals that the determinations of Maass and Hatcher[2] reported at both 0 and 18° are the most accurate data available. Independent verification of the data, however, has not appeared, and independent values in the region of high peroxide concentration are particularly desirable in view of the surface activity of the glass unless very special precautions are taken.

In this investigation a technique has been developed for preparing vessels whose interior surfaces are insensitive toward the decomposition of peroxide, determining with precision the densities of aqueous solutions of hydrogen peroxide at 0°. The mean coefficient of change of density with temperature to 20° has also been measured.

Treatment to Render Glassware Inactive to Hydrogen Peroxide.—The following procedure was found to produce inactive container Pyrex glass surfaces.

All glassware was constructed of Pyrex tubing, selected for freedom from visible surface imperfections. Prior to the glassblowing the tubing was cleaned with hot fuming sulfuric acid (150–175°), rinsed with conductivity water, and allowed to drain until dry in a dust-free case. This treatment is important in that it removes foreign matter which might otherwise decompose or "ash" and become embedded in the surface of the glass during the glassblowing operation. The air required in the glassblowing was passed through a filter of fresh medicinal cotton to prevent contamination through air-borne dust or decomposition of organic vapors from the breath.

After the vessels had been constructed, they were filled with hot fuming sulfuric acid and allowed to stand overnight. Following thorough rinsing with conductivity water, the vessels were tested with 90–95% peroxide. If no bubbles of oxygen appeared, the vessels were ready for use.

In the few instances where decomposition was detected,

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(1) The authors express their acknowledgment to the Naval Bureau of Ordnance for the support and release of this work.

(2) O. Maass and W. H. Hatcher, THIS JOURNAL, **42**, 2548 (1920).

the peroxide was removed and the vessels re-rinsed with conductivity water. Then the vessels were treated with 10% hydrofluoric acid for three or four minutes. If, after this treatment had been repeated several times, the vessel still decomposed the peroxide, it was concluded that some foreign matter was deeply embedded in the surface of the vessel and the vessel was discarded.

Although precautions were taken to keep the vessels in a dust-free place, occasionally a vessel would become contaminated between times of use. This contamination, however, was always successfully removed by repeating the cleaning procedure with fuming sulfuric acid, hydrofluoric acid, and conductivity water. It was also found that the tendency of the vessels to become contaminated was reduced by keeping them filled with concentrated peroxide when not in use.

It has been found that cleaning a vessel with chromate-sulfuric acid cleaning solution usually increased rather than decreased the catalytic action of the vessel toward the decomposition of the peroxide.

Density Determinations at 0°

Experimental Procedure for Measuring Densities.—The densitometers consisted of Erlenmeyer-type glass bulbs of about 20 cc. capacity, to which was attached a short section of 2 mm. capillary tubing, and to which in turn was attached a ground glass cap. At a point at mid-distance along the capillary, a small scratch or level mark was made on the capillary tubing.

Calibration of the volume at 0° of the densitometers was carried out with conductivity water at 0°. The densitometer was filled with water to a level somewhat above the mark and placed in an ice-bath for approximately forty-five minutes. Tests showed that this time was more than sufficient to reduce the temperature of the water in the densitometer to 0°. The liquid level was finally adjusted to the mark by removing the excess liquid with a fine capillary. Any small drops of liquid clinging to the walls of the capillary above the mark were removed by using a fine capillary tube connected to a water aspirator.

The densitometer was transferred from the ice-bath to a water-bath at room temperature to warm the densitometer and contents quickly to room temperature in preparation for weighing. The densitometer was removed from the water-bath, dried and weighed. The precision of the calibrations was in round numbers a part in 10,000.

In making density determinations, the densitometers were filled with peroxide which had been twice distilled to ensure purity. The same manipulations were employed as were followed in the calibrations. Thus having determined the weight of a known volume of the peroxide solution at 0°, the density at 0° could be calculated easily. The precision of the density measurements was close to a part in 10,000.

Analytical Procedure

After density weighing, samples of peroxide for analysis were withdrawn by means of a capillary pipet constructed and treated according to previous indications relative to the densitometers. In a previous investigation,[3] it has been shown that the analysis of aqueous solutions of hydrogen peroxide can be carried out with great accuracy by titration with potassium permanganate provided a definite procedure is followed. To achieve the maximum possible accuracy, both the standardization of the permanganate and the titration of the peroxide were carried out according to the recommendations given in the reference cited.

To analyze concentrated peroxide solutions by titration with permanganate, a dilution step is necessary. All quantities of material involved in the dilutions were determined by weighing rather than by the less accurate volumetric method. Weight burets were also used for the titrations. The precision of the analyses was not inferior to a part in 5000.

An attempt was made to determine directly the amount of impurities in the best obtainable grade of sodium oxalate[4] used to obtain the titer of the potassium permanganate by comparing the oxalate with purified anhydrous oxalic acid. Although the oxalic acid was sublimed in high vacuum eight times, for some undetermined reason the results showed a lack of uniformity to a part in 800.

The same oxalate as used in the comparison of the permanganate titration with the decomposition method was also used in the density determinations. The results of the earlier comparisons[2] by direct peroxide decomposition indicated that the oxalate purity is not inferior to a part in 3500. It is believed that the concentration determinations are reliable to a part in 5000.

Experimental Results

The experimental results of the density determinations at 0° are given in Table I.

TABLE I

DENSITIES OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AT 0°

Weight fraction of water	Density at 0°, g. per cubic cm.	Weight fraction of water	Density at 0°, g. per cubic cm.
0.90343	1.0379	0.10621	1.4100
.80021	1.0803	.04013	1.4483
.59991	1.1660	.03772	1.4493
.40829	1.2539	.03718	1.4499
.28646	1.3139	.00521	1.4681
.19977	1.3590	.00395	1.4685

An attempt to express the data algebraically showed that no simple function would represent the densities as a function of weight fraction or mole fraction with sufficient precision. An equation of the following form was found to be the best approximation representation.

$$\log v_{\mathrm{m}} = \log v_{\mathrm{H_2O_2}} + \log (v_{\mathrm{H_2O}}/v_{\mathrm{H_2O_2}})x \qquad (1)$$

where

v_{m} represents specific volume of H_2O_2 solution cc./g.
$v_{\mathrm{H_2O_2}}$ represents the specific volume of 100% H_2O_2 cc./g.
$v_{\mathrm{H_2O}}$ represents the specific volume of H_2O cc./g.
x represents the weight fraction of water

or

$$\log [(v_{\mathrm{m}})(10)] = 0.83241 + 0.16767x \qquad (1a)$$

The deviation of the data from this curve exhibits a maximum with a value of about a part in 400. Since representing the data algebraically to a part in 5000 appeared impractical, a table of densities for each 0.01 interval of weight fraction was prepared with the aid of a deviation chart. The density values are given in Table II, and the specific volumes in Table II R.

Linear interpolation between the values given in Table II is accurate to at least a part in 5000 as illustrated in Table III.

The interpolated densities were obtained by linear interpolation using the tabulated values of Table II. The calculated densities were obtained from Equation (1a) corrected by the use of the deviation plot.

The comparison of the results of this investigation with those reported by Maass and Hatcher[1] is shown in Table IV.

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[3] C. E. Huckaba and F. G. Keyes, THIS JOURNAL, **70**, 1640 (1948).

[4] A portion of this oxalate is being preserved and is available for further investigation.

TABLE II

DENSITIES IN VACUUM, G. PER CC., OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AT 0°, AS A FUNCTION OF THE WEIGHT

	Fraction of water									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	1.4709	1.4651	1.4593	1.4535	1.4478	1.4421	1.4364	1.4307	1.4250	1.4193
.1	1.4136	1.4080	1.4024	1.3968	1.3913	1.3858	1.3804	1.3750	1.3696	1.3642
.2	1.3589	1.3536	1.3483	1.3430	1.3378	1.3326	1.3275	1.3223	1.3172	1.3121
.3	1.3071	1.3022	1.2971	1.2921	1.2871	1.2822	1.2773	1.2724	1.2676	1.2627
.4	1.2579	1.2531	1.2483	1.2436	1.2389	1.2342	1.2295	1.2248	1.2202	1.2156
.5	1.2110	1.2064	1.2018	1.1973	1.1928	1.1883	1.1838	1.1793	1.1749	1.1705
.6	1.1661	1.1617	1.1573	1.1529	1.1485	1.1441	1.1398	1.1355	1.1312	1.1269
.7	1.1226	1.1183	1.1140	1.1098	1.1056	1.1014	1.0972	1.0930	1.0888	1.0846
.8	1.0804	1.0763	1.0722	1.0680	1.0639	1.0598	1.0557	1.0516	1.0475	1.0434
.9	1.0393	1.0353	1.0313	1.0273	1.0233	1.0193	1.0154	1.0115	1.0076	1.0037
1.0	0.9998									

TABLE IIR

SPECIFIC VOLUMES G. PER CC. OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AT 0°, AS A FUNCTION OF THE WEIGHT FRACTION OF WATER

	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.67986	0.68255	0.68526	0.68799	0.69070	0.69343	0.69618	0.69896	0.70175	0.70457
.1	.70741	.71023	.71306	.71592	.71875	.72160	.72443	.72727	.73014	.73303
.2	.73589	.73877	.74167	.74460	.74750	.75041	.75330	.75626	.75919	.76214
.3	.76505	.76793	.77095	.77393	.77694	.77991	.78290	.78592	.78889	.79195
.4	.79498	.79802	.80109	.80412	.80717	.81024	.81334	.81646	.81954	.82264
.5	.82576	.82891	.83209	.83521	.83836	.84154	.84474	.84796	.85114	.85434
.6	.85756	.86081	.86408	.86738	.87070	.87405	.87735	.88067	.88402	.88739
.7	.89079	.89421	.89767	.90106	.90449	.90794	.91141	.91491	.91844	.92200
.8	.92558	.92911	.93266	.93633	.93994	.94357	.94724	.95093	.95465	.95841
.9	.96219	.96590	.96965	.97343	.97723	.98107	.98483	.98863	.99246	.99631
1.0	1.00020									

TABLE III

ACCURACY OF LINEAR INTERPOLATION IN TABLE II

Wt. fraction of water	Interpolated density	Calculated density
0.105	1.4108	1.4106
.505	1.2087	1.2087
.905	1.0373	1.0374

TABLE IV

COMPARISON OF DENSITIES OBTAINED BY MAASS AND HATCHER WITH THOSE IN THIS INVESTIGATION

Density at 0°	Weight fraction water	
Maass and Hatcher	Maass and Hatcher	Huckaba and Keyes
1.0419	0.8943	0.8938
1.0894	.7767	.7783
1.1655	.5986	.6014
1.2404	.4330	.4368
1.2610	.3880	.3935
1.3235	.2656	.2677
1.3839	.1514	.1535
1.4144	.0958	.0984
1.4596	.0111	.0202
1.4649	.0000	.0105

The densities reported by Maass and Hatcher are lower than the ones reported here. These investigators reported great difficulty in eliminating decomposition of the peroxide during the density measurements. However during the measurements here reported no visible decomposition occurred. It will be perceived that if decomposition occurs during a density measurement, the value obtained will be lower than the true value.

The Change of Density with Temperature.—The effect of temperature on the densities of peroxide solutions was found by using a dilatometer constructed to permit the observation of expansions of volume of solutions from 0 to 20°. The dilatometer differed from the densitometer only in that the capillary section was much longer (9.5 cm.) and accurately divided into millimeters and calibrated. The diameter of the capillary section was obtained by determining the amount of mercury at a known temperature that filled the space between successive portions of the millimeter division marks. The first mark above the bulb of the dilatometer was taken to be the zero mark, and the total volume of the dilatometer from this mark was determined with conductivity water in the same manner as with the simpler densitometers. The following procedure was used in making a dilatometer measurement.

The density of the peroxide solution was determined at 0° by adjusting the liquid level to the zero mark following the same procedure used earlier. From the density at 0°, the concentration was established from Table II. The dilatometer was then placed in a 20° bath, and after equilibrium had been attained, the new liquid level was read. To ensure that the reading was made at equilibrium the level was observed twice by approaching the 20°[5] from both a lower and a higher temperature. From the level reading and the diameter of the capillary tube, the volume of liquid at 20° above the zero mark was calculated. The volume of liquid below the zero mark was corrected from 0 to 20° using the coefficient of cubical expansion of Pyrex glass. Thus, the total volume at 20° of a known weight of peroxide and also the density at 20° are determined.

Since an adequate correlation of the volumetric coefficients with weight fractions of hydrogen peroxide is possible, the coefficients of change are presented on a specific volume rather than density basis. The average coefficients of expansion between 0 and 20° to be listed were obtained by using the data to determine the constant α of Equation (2).

$$v_{t_2} = v_{0°\text{C}}\,(1 + \alpha\Delta t) \qquad (2)$$

TABLE V

AVERAGE COEFFICIENTS OF CHANGE IN SPECIFIC VOLUME OF HYDROGEN PEROXIDE SOLUTIONS BETWEEN 0 AND 20°

Weight fraction water	α
0.03123	0.0007759
.21471	.0007344
.40917	.0006656
.60841	.0005846
.78475	.0004326
1.00000	.0001206

TABLE VI

COMPARISON OF COMPUTED AND EXPERIMENTAL SPECIFIC VOLUMES

Weight fraction water	v exptl. at 20°	v calcd. at 20°
0.78475	0.92818	0.92826
.60841	.87037	.87006
.40917	.80836	.80836
.21471	.75103	.75101
.03123	.69888	.69918

where

v represents specific volume cc./g.
Δt represents change in temperature (t_2 − 0°)
α represents average coefficient of expansion between 0° and t_2

The experimental results are given in Table V.

The relationship between α and weight fraction is adequately represented by the expression

$$\alpha = \frac{\log\,[(1.10344 - x)(10)] + 0.16908}{1523} \qquad (3)$$

where

x = weight fraction water
α = average coefficient of change in specific volume between 0 and 20°

A comparison of the specific volumes at 20° computed from the coefficients using Equation (3) with the direct experimental specific volumes is shown in Table VI. The differences are negligible in each case, demonstrating the adequacy of Equation (3).

For convenience, the coefficients have been calculated using Equation (3) for each 0.01 interval of weight fraction, and appear in Table VII. Linear interpolation in this table is satisfactory.

To determine the specific volume at some temperature, t_2, intermediate 0 and 20° of a hydrogen peroxide solution, subject to the assumption of temperature independence of α, the specific volume at 0° is obtained from Table II; α is then either obtained from Table VII or calculated by Equation (3); and finally the specific volume at t_2 obtained by the use of Equation (2).

TABLE VII

AVERAGE COEFFICIENTS OF SPECIFIC VOLUME CHANGB[a] FROM 0–20° OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AS A FUNCTION OF THE WEIGHT FRACTION OF WATER

The entries of the table are to be multiplied by 10^{-4}.

	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	7.957	7.931	7.905	7.878	7.852	7.825	7.797	7.770	7.742	7.714
.1	7.685	7.657	7.629	7.599	7.570	7.540	7.510	7.480	7.449	7.418
.2	7.387	7.355	7.323	7.290	7.258	7.224	7.191	7.157	7.122	7.087
.3	7.052	7.016	6.980	6.944	6.906	6.869	6.831	6.792	6.753	6.713
.4	6.673	6.632	6.591	6.549	6.506	6.463	6.419	6.374	6.329	6.283
.5	6.236	6.188	6.140	6.090	6.040	5.989	5.937	5.884	5.830	5.775
.6	5.719	5.662	5.604	5.544	5.483	5.421	5.357	5.292	5.226	5.158
.7	5.088	5.016	4.943	4.867	4.790	4.710	4.629	4.544	4.457	4.368
.8	4.275	4.180	4.081	3.979	3.872	3.762	3.647	3.528	3.403	3.272
.9	3.135	2.992	2.840	2.680	2.511	2.331	2.139	1.933	1.711	1.470
1.0	1.206									

[a] This coefficient, designated herein as α, is defined by Equation (2).

Summary

The densities of aqueous solutions of hydrogen peroxide at 0° have been determined with a precision of a part in 5000. The coefficients of change with temperature in these densities have been determined from 0 to 20° with a precision such that densities calculated using the coefficients also have a precision of a part in 5000.

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[5] The mercury thermometer used in the 20° temperature bath could be estimated to 0.01°, and was checked against a platinum resistance thermometer.