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THE PREPARATION AND SPECIFIC GRAVITY OF PURE FORMIC
ACID AND ITS AQUEOUS SOLUTIONS.

BY

LEO HENRY MERCHIE.

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
MASTER OF SCIENCE IN CHEMISTRY

Rolla, Mo.

1933.

Approved by

A. L. Deuelok

Professor of Chemical Engineering.

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TABLE OF CONTENTS.

	Page
INTRODUCTION.....	1
METHODS OF PREPARING ANHYDROUS FORMIC ACID.....	2
PROCEDURE.....	4
TABLE I (Analysis of Formic Acid and its Aqueous Solutions.).....	9
TABLE II (Specific Gravity of Pure Formic Acid and its Aqueous Solutions.).....	16
DISCUSSION OF DATA.....	17
BIBLIOGRAPHY.....	19
INDEX.....	22

LIST OF ILLUSTRATIONS.

	Between Pages
Fig. I. (Pressure-Temperature Curves of Formic Acid and Water.).....	6-7
Fig. II. (Diagram of Apparatus.).....	6-7
Fig. III. (Diagram of Pycnometer.).....	9-10
Fig. IV. (Specific Gravity-Percentage Curves for Aqueous Solutions of Formic Acid.).....	17-18

INTRODUCTION

Formic acid, the lowest member of the fatty acid series, was obtained as early as the seventeenth century by distilling ants with water. Other methods were later found after the correct constitution of the acid became known. This acid is not difficult to prepare in a water solution, but it is difficult to obtain in the anhydrous state.

The anhydrous acid is very hygroscopic and absorbs water from the air very readily. This water cannot be separated by distillation at atmospheric pressure because there is only a fraction of a degree difference between the boiling points of water and formic acid. If strong dehydrating agents, such as sulphuric acid or phosphorus pentoxide are used, the formic acid decomposes into water and carbon monoxide. From the structure of formic acid, it will be seen that it is easily oxidized as it has an aldehyde group. For this reason this acid is often used as a reducing agent.

Anhydrous formic acid can not be obtained from manufacturers of organic chemical compounds. The best C.P. acid contains 10% to 15% water, while other grades have considerably higher water content.

Due to this difficulty of obtaining anhydrous

formic acid there is considerable conflict in data on the true specific gravity of anhydrous formic acid. Many different values for the specific gravity of the pure acid and various dilutions of the acid in water are given in the literature,¹ by various authors. Much of the data given in the literature was obtained several years ago and the methods used for securing it might be seriously questioned as to their accuracy. Extreme care must be exercised in order to keep the acid anhydrous after it has once been obtained.

The purpose of this work is to study the various methods of preparing anhydrous formic acid, to improve a method for preparing the anhydrous acid, and to correct specific gravity tables for aqueous solutions of formic acid.

METHODS OF PREPARING ANHYDROUS FORMIC ACID.

Many methods for preparing anhydrous formic acid are given in the chemical literature. The method of passing dry hydrogen sulfide gas over anhydrous lead formate was used by Richardson and Allaire.² This method is objectionable because of the ease by which sulfur may contaminate the acid and perhaps form thio acids which would easily increase the specific gravity, also

hydrogen sulfide is quite soluble in formic acid, as the formic acid has a very high dielectric constant and also resembles water in many other of its characteristics. Sapojnikoff,³ Tessarin,⁴ Ewins,⁵ and others used fractional crystallization for preparing anhydrous formic acid. It is very difficult to carry out any fractional recrystallization with a very hygroscopic substance and water free compounds prepared by this method are extremely questionable. Jones⁶ used phosphorus pentoxide and suggests the use of a fractionating column under reduced pressure. Garner, Saxton, and Parker⁷ used anhydrous copper sulphate and distillation under reduced pressure. This method has an advantage in that it is entirely out of contact with the air and assuming the dehydrating material is reasonably efficient, it seemingly gives promise of approaching the desired end fairly closely. Many German⁸ commercial patents use sulphuric acid, orthophosphoric acid, acid salts and various anhydrous salts that tend to take up water of crystallization.

Many of the above methods claim to produce anhydrous formic acid while others only give 98% to 99.5% acid. Some of the methods cause considerable decomposition of the acid. None of the papers give a very clear

description of the whole method of procedure, and in many cases much was seemingly taken for granted.

PROCEDURE

The method of Richardson and Allaire² has been used in the laboratory here several times and gave an inferior quality of acid and poor yields.

The method of fractional crystallization is slow and difficult and gives poor separation, since it is very difficult to completely separate the mother liquor from the formic acid crystals. In using this method, acid of about 97% concentration was obtained after five recrystallizations.

The phosphorus pentoxide method causes much decomposition of the formic acid when added without agitation. To avoid this, an electric stirrer was used to rapidly mix this dehydrating agent with the acid. Phosphorus pentoxide is a very energetic dehydrating agent. If this oxide can not come in contact with the water in the acid, it will take it from the formic acid and evolve carbon monoxide especially when there is slight local overheating. Then, the phosphoric acid formed has quite an affinity for the formic acid as the latter resembles water somewhat in being a good solvent

for the phosphoric acid. Then to distill out the formic acid causes some decomposition, thus yielding an acid not entirely devoid of water. The formic acid was first cooled in an ice bath and the phosphorus pentoxide added in very small quantities. The resulting mixture then was distilled under reduced pressure and the acid condensed with ice water through the condenser. The best acid obtained by this method was about 98% formic acid, but considerable amount of acid was lost by decomposition with the phosphorus pentoxide.

Fractional distillation under reduced pressure from a 500 cc. flask containing approximately 300 cc. of about 95% acid, gave small yields of 99.5% acid. The fractionating column was a straight column two feet in length, one inch in diameter and filled with half inch lengths of small glass tubing. Glass beads were tried as filler but seemed to cause too much condensation and prevented return of the condensate to the flask.

The same apparatus and method used in the phosphorus pentoxide method was employed with sulphuric acid as the dehydrating agent. In this case the formic acid was almost completely decomposed.

The method of Garner, Saxton, and Parker⁷ was tri-

ed and found to be very slow. Four distillations from anhydrous copper sulphate at 120 mm. pressure produced an acid of about 98% concentration. This pressure is not low enough for good separation if the pressure curves of water and formic acid given by Jones⁶ are accurate. This work seems to verify the work of Jones⁶ as to the vapor pressure and temperature of formic acid and water. These curves are reproduced in Fig. I.

From studying these various methods a modified method was developed which makes use of a fractionating column and anhydrous copper sulphate. 100% acid was produced after two distillations from an original sample of C.P. 90% acid. A diagram of the apparatus is shown in Fig. II.

The following is a description of the apparatus and procedure used for the preparation of anhydrous formic acid. An electric heater (A) was used when heat was required for the distillation. The formic acid solution with enough anhydrous copper sulphate to fill the lower fourth of the flask was introduced into the flask (B). The acid was distilled through the fractionating column (C) which was filled with half inch lengths of small glass tubing and was surrounded by a condenser through which water from 18^o-20^o C. was cir-

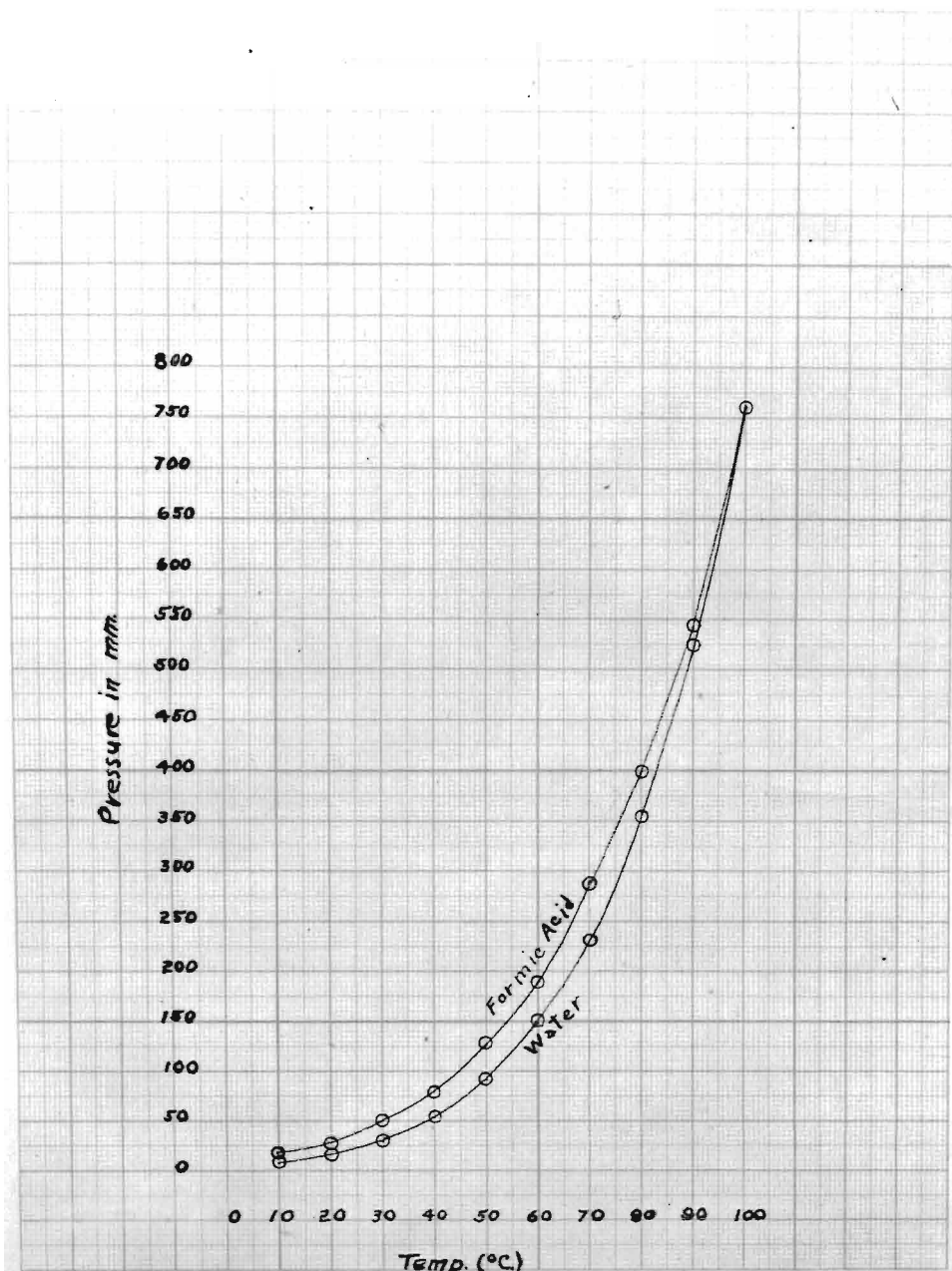


Fig. I.

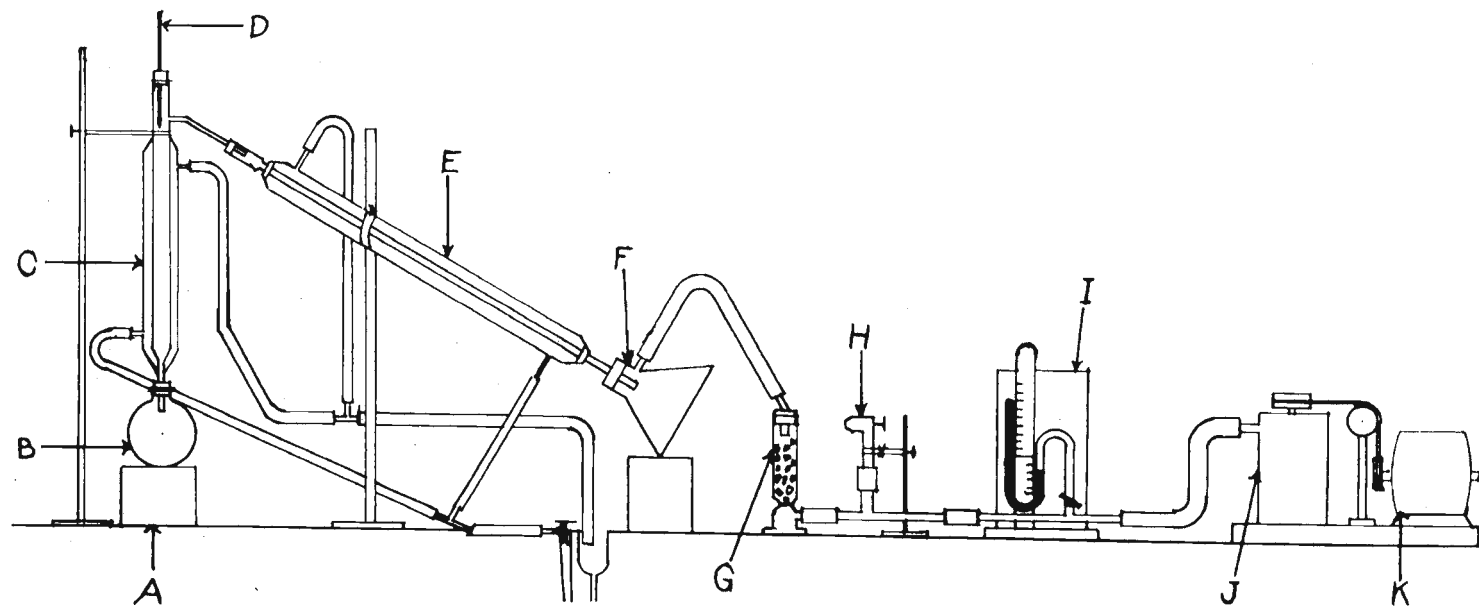


Fig. II.

culated. The distillation was carried on at a pressure of 29-31 mm. of mercury at which pressure the boiling point of formic acid is about 20°C . and the boiling point of water is about 30°C . as shown in Fig. I. The water condensed in the column and dropped back into the flask where it was taken up by the anhydrous copper sulphate. Most of the formic acid passed up the column, around the thermometer (D), out the side neck and into the condenser (E) which had water at about 18°C . circulating in it. The liquid acid was collected in the side neck flask (F). A calcium chloride tower (G) kept out moisture when the pressure was released in the system. The vacuum pump was kept running continuously and the pressure was controlled by admitting small amounts of air by the needle valve (H) which was constructed from the bottom part of a Bunsen burner. The pressure was read on the manometer (I) and the vacuum in the system was produced by an oil vacuum pump (J).

The anhydrous copper sulphate was prepared as follows: Powdered copper sulphate pentahydrate was gradually heated in an iron pan to 155°C . with frequent stirring. The final dehydration was completed by holding the temperature at 155°C . for one half hour and having approximately 1 cm. layer in the iron pan. This

hot copper sulphate was transferred to a ground glass stoppered bottle for cooling. Fresh lots were prepared as used and not permitted to stand for any length of time.

The acid produced by this method had a boiling point of 20°C . at 30 mm. pressure and a specific gravity of 1.2200 at 20°C .

Upon comparing this specific gravity with the data given in the International Critical Tables⁹ there was found to be considerable difference. This lead to the investigation of specific gravities of water solutions of formic acid.

The percent of formic acid in these solutions, as well as of the anhydrous acid, was determined by titrating a carefully weighed sample with an approximately tenth normal sodium hydroxide solution, using phenolphthalein as an indicator. The formic acid was weighed out in stoppered weighing bottles, opened under carbon dioxide free water and immediately titrated.

The carbonate in the sodium hydroxide was separated out by precipitating with barium chloride and then siphoning off the clear solution. The sodium hydroxide was then standardized against both oxalic acid and standard sulphuric acid.

The specific gravities were determined with the pycnometer shown diagrammatically in Fig. III. This pycnometer was made of thick walled capillary glass tubing and fitted with a ground glass stopper and had a capacity of about 1 cc. of distilled water at 20°C. The specific gravities were all taken at 20°C. and compared to water at 4°C. The pycnometer filled with the acid was placed in a constant temperature bath until the pycnometer and its contents came to the temperature of the bath.

The following table shows the results obtained by titration:

TABLE I.

Analysis of Formic Acid and its Aqueous Solutions.

Weight of HCOOH taken in gm.	cc. of NaOH used	% HCOOH in sample	Average % HCOOH
	.1238N NaOH		
.2537	44.53	99.99	100.00
.3150	55.30	100.01	
.2648	46.45	99.93	99.93
.2530	44.38	99.93	
.2566	44.92	99.73	99.73
.2142	37.50	99.73	

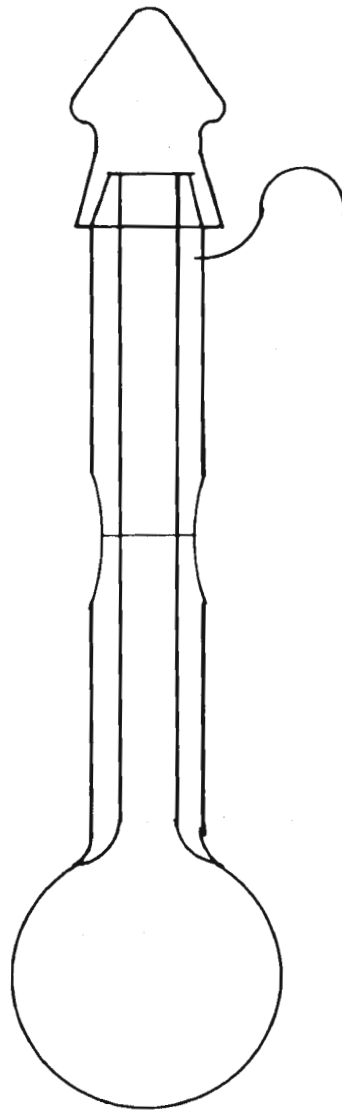


Fig. III.

Weight of HCOOH taken in gm.	cc. of NaOH used	% HCOOH in sample	Average % HCOOH
	.1377N NaOH		
.2223	34.90	99.49	99.515
.2209	34.70	99.54	
	.1136N NaOH		
.2891	54.75	99.01	98.99
.2583	48.90	98.97	
.3338	62.95	98.59	98.605
.2563	48.35	98.62	
	.1377N NaOH		
.2461	38.27	98.54	98.565
.2137	33.25	98.59	
.2427	37.60	98.17	98.20
.2556	39.62	98.23	
.2520	38.97	98.01	98.02
.2508	38.80	98.03	
	.1136N NaOH		
.2592	48.45	97.72	97.72
.2525	47.20	97.72	
	.1377N NaOH		
.2408	37.05	97.50	97.495
.2132	32.80	97.49	

Weight of HCOOH taken in gm.	cc. of NaOH used	% HCOOH in sample	Average % HCOOH
.1762	27.07	97.35	97.345
.2168	33.30	97.34	
.1136N NaOH			
.2882	53.52	97.09	97.10
.1973	36.65	97.11	
.2611	48.30	96.71	96.69
.2485	45.95	96.67	
.1377N NaOH			
.2730	41.65	96.68	96.675
.2379	36.45	96.67	
.2575	39.25	96.59	96.61
.2033	31.00	96.63	
.1136N NaOH			
.2896	53.50	96.58	96.51
.2613	48.20	96.44	
.1377N NaOH			
.2213	33.70	96.50	96.495
.1957	29.80	96.49	
.0765N NaOH			
.2296	62.80	96.46	96.425
.1629	44.60	96.39	

Weight of HCOOH taken in gm.	cc. of NaOH used	% HCOOH in sample	Average % HCOOH
	.1377N NaOH		
.1982	30.08	96.17	96.215
.1797	27.30	96.26	
	.0765N NaOH		
.2293	62.60	96.11	96.135
.3372	92.10	96.16	
	.1377N NaOH		
.2270	34.40	96.03	96.06
.2595	39.35	96.09	
	.0765N NaOH		
.2317	63.15	95.95	95.955
.2003	54.60	95.96	
	.1377N NaOH		
.2223	33.55	95.64	95.66
.2328	35.15	95.68	
	.1136N NaOH		
.3783	69.10	95.49	95.515
.2331	42.60	95.54	
	.0765N NaOH		
.1989	53.92	95.44	95.41
.2340	63.40	95.38	

Weight of HCOOH taken in gm.	cc. of NaOH used	%HCOOH in sample	Average % HCOOH
.2412	65.23	95.21	95.24
.2355	63.73	95.27	
.2246	60.70	95.14	95.11
.2392	64.60	95.08	
.1377N NaOH			
.2361	35.30	94.74	94.74
.1672	25.00	94.74	
.0765N NaOH			
.2342	62.77	94.36	94.41
.2019	54.20	94.46	
.2992	80.15	94.31	94.28
.1692	45.30	94.25	
.1377N NaOH			
.1949	29.00	94.28	94.245
.2324	34.55	94.21	
.1981	29.40	94.04	94.035
.2143	31.80	94.03	
.0765N NaOH			
.2345	62.40	93.68	93.675
.1663	44.25	93.67	

Weight of HCOOH taken in gm.	cc. of NaOH used	% HCOOH in sample	Average % HCOOH
	.1377N NaOH		
.2263	33.35	93.39	93.41
.2289	33.75	93.43	
.2128	31.30	93.21	93.19
.2310	33.95	93.17	
.2395	35.15	93.00	93.005
.2482	36.43	93.01	
.2028	29.65	92.64	92.63
.2381	34.80	92.62	
.2010	29.35	92.53	92.54
.1941	28.35	92.55	
.2000	29.05	92.04	92.04
.2630	38.20	92.04	
	.1424N NaOH		
.2132	29.80	91.60	91.615
.2503	35.00	91.63	
.1990	27.75	91.38	91.375
.2001	27.90	91.37	
.2218	30.80	91.00	91.005
.2045	28.40	91.01	
.2032	28.13	90.72	90.71
.2200	30.45	90.70	

Weight of HCOOH taken in gm.	cc. of NaOH used	% HCOOH in sample	Average % HCOOH
.1969	27.17	90.42	
.1932	26.67	90.46	90.44
.2809	38.60	90.05	
.2510	34.50	90.07	90.06
.2454	33.65	89.86	
.2570	35.25	89.88	89.87
.2334	31.80	89.28	
.1787	24.35	89.29	89.285
.1649	22.37	88.90	
.2173	29.50	88.96	88.93

From the preceding table it will be seen that in most cases the difference in percent between two samples was very small and well within the limits of measurement.

The next table shows the specific gravities determined for these samples. The average percent for each sample was used in this table and the specific gravities were determined by the method given previously. In all cases the specific gravities were checked exactly to the fourth decimal figure.

TABLE II.

Specific Gravity of Pure Formic Acid and its Aqueous
Solutions at $\frac{20^{\circ}}{4^{\circ}}$ C.

% HCOOH	SPECIFIC GRAVITY	% HCOOH	SPECIFIC GRAVITY
100.00	1.2200	96.42	1.2156
99.93	1.2198	96.21	1.2152
99.73	1.2194	96.13	1.2150
99.51	1.2189	96.06	1.2145
98.99	1.2185	95.95	1.2140
98.61	1.2181	95.66	1.2132
98.56	1.2180	95.51	1.2129
98.20	1.2176	95.41	1.2127
98.02	1.2174	95.24	1.2124
97.72	1.2171	95.11	1.2121
97.49	1.2169	94.74	1.2114
97.34	1.2167	94.41	1.2110
97.10	1.2164	94.28	1.2107
96.69	1.2160	94.24	1.2107
96.67	1.2160	94.03	1.2103
96.61	1.2159	93.67	1.2096
96.51	1.2158	93.41	1.2090
96.49	1.2158	93.19	1.2086

% HCOOH	SPECIFIC GRAVITY	% HCOOH	SPECIFIC GRAVITY
93.00	1.2084	90.71	1.2048
92.63	1.2078	90.44	1.2044
92.54	1.2077	90.06	1.2039
92.04	1.2070	89.87	1.2037
91.61	1.2066	89.28	1.2029
91.37	1.2061	88.93	1.2022
91.00	1.2056		

These results are plotted in Fig. IV. and compared to the results of plotting the figures given in the International Critical Tables.⁹ The figures given in the International Critical Tables are those of Richardson and Allaire.²

DISCUSSION OF DATA.

From the data found and from the graph plotted, it seems that it is necessary to obtain readings very close together in order to obtain a very accurate specific gravity table for formic acid. This was not done in the case of the table constructed by Richardson and Allaire,² only seventy-seven points being determined.

The specific gravity of the anhydrous formic acid

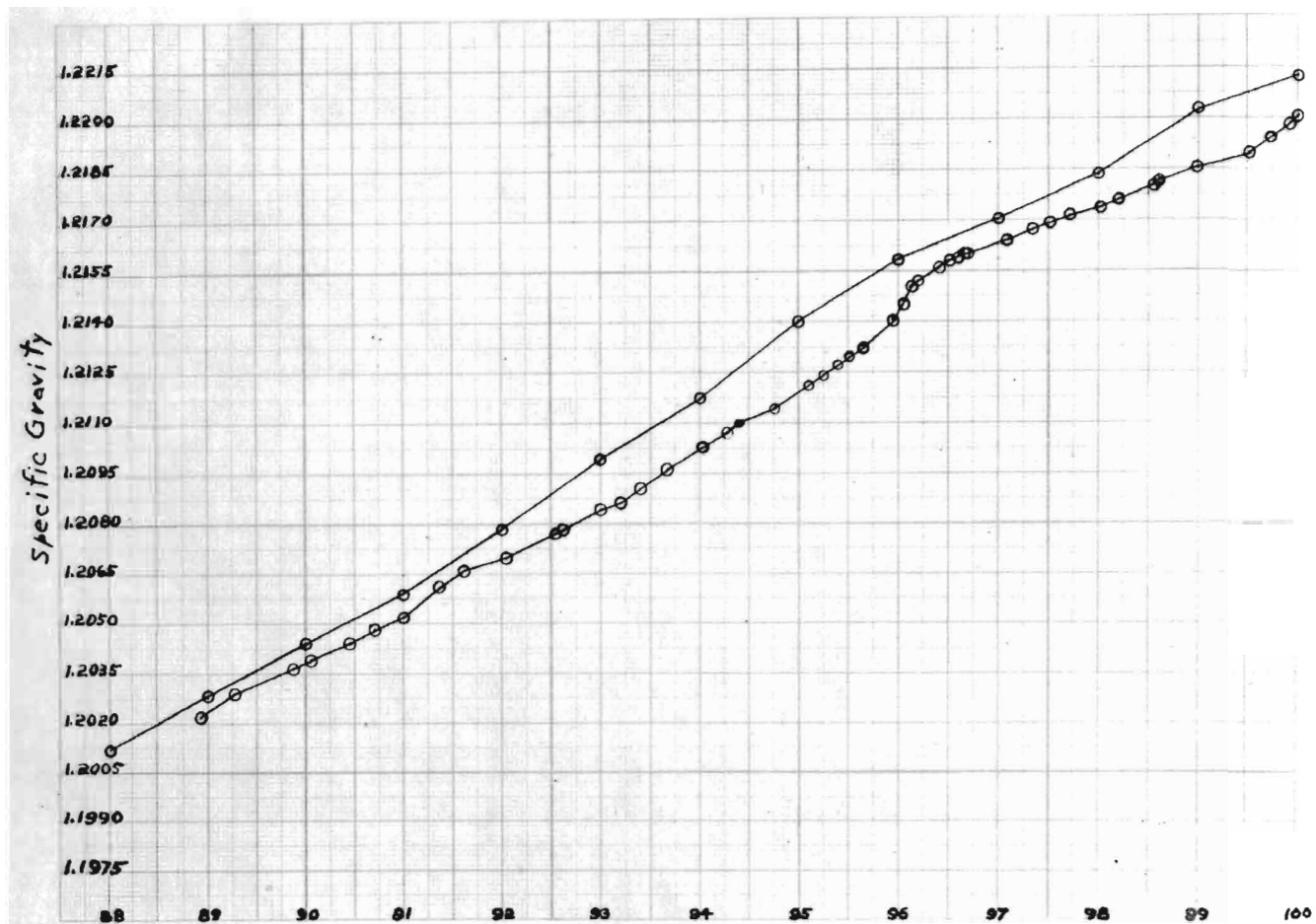


Figure IV Percent Formic Acid

obtained during this work was considerably lower than the value given by Richardson and Allaire,² but agrees with the value given by Garner, Saxton, and Parker.⁷

There seems to be considerable chance that the method of preparation used by Richardson and Allaire² would lead to impurities in the acid and give a higher specific gravity. Since no volatile impurities are introduced in the method developed during this work a more pure acid should be produced. The care used in weighing and titrating samples and in taking specific gravities reduces to a minimum the chances for errors due to these operations.

From the procedure employed and the data obtained in this work, the value given by Garner, Saxton, and Parker⁷ and the one given in this paper appears to be the correct specific gravity for anhydrous formic acid. The specific gravities for the water solutions also appear to be more accurate than those of Richardson and Allaire.²

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INDEX

A	
Allaire, P.	2, 4, 17, 18, 19, 20
B	
Bibliography	19
C	
Chem. Fabrik Griesheim Elektron	21
Chemische Fabrik Gruinau	21
D	
Discussion of Data	17
E	
Ewins, A. J.	3, 20
F	
Fig. I.	6
Fig. II.	6
Fig. III.	9
Fig. IV.	17
G	
Garner, J. B.	3, 5, 18, 20, 21
H	
Homfray, Ida F.	19

I

International Critical Tables	8, 17, 21
Introduction	1

J

Jones, D. C.	3, 6, 21
-------------------	----------

M

Methods of Preparing Anhydrous Formic Acid	2
--	---

P

Parker, H. O.	3, 5, 18, 20, 21
Procedure	4

R

Richardson, G. M.	2, 4, 17, 18, 19, 20
------------------------	----------------------

S

Sapojnikoff, V.	3, 20
Saxton, B.	3, 5, 18, 20, 21

T

Table I.	9
Table II.	16
Tessarini, H. Z.	3, 19, 20
Traube, J.	19