- (13) Mellanby, E., and Green, H. N., Brit. Med. J., 1, 984 (1929).
- (14) Metropolitan Life Insurance Co., Statistical Bull. 4, 1923.
 (15) Mills, A. B., "Extent of Illness and of Physical and Mental Defects Prevailing in the United States," Committee on Cost of Medical Care, Washington, D. C., 1929.
- (16) Osborne, T. B., and Mendel, L. B., Am. J. Physiol., 69, 543 (1924).
- (17) Pharmacopeia of the United States, 10th Decennial Revision, Lippincott, 1926.
- (18) Prather, E. O., Nelson, M., and Bliss, A. R., Am. J. Diseases Children, 42, 52 (1931).
- (19) Sherman, H. C., "Chemistry of Food and Nutrition," Macmillan, 1926.
- (20) Sherman, H. C., and Burtis, M. P., Proc. Soc. Exptl. Biol. Med., **25**, 649 (1928).
- Sherman, H. C., and MacLeod, F. L., J. Am. Chem. Soc., 47, 1658 (1925).
- Shurley, B. R., and Turner, R. G., J. Am. Med. Assoc., 94,
- Sydenstricker, E., Pub. Health Repts., Reprint 1172 (1927).
- Turner, R. G., J. Infectious Diseases, 45, 208 (1929); Proc. Soc. Exptl. Biol. Med., 26, 233 (1928). (25) Werkman, C. H., J. Infectious Diseases, 32, 255 (1923).
- (26) Yudkin, A. M., J. Am. Med. Assoc., 79, 2206 (1922).

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Glycerol Viscosity Tables

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OTWITHSTANDING some statements in the literature to the effect that glycerol and its aqueous solutions are not entirely suitable liquids for use as viscosity standards in calibrating technical viscometers, these solutions have come into common use for this purpose. The principal objection offered against them lies in the fact that solutions above approximately 85 per cent glycerol are hygroscopic, whereas those below this concentration give up water when exposed to average humidity conditions. Experience has shown that these properties do not offer serious difficulties if the facts are recognized and precautions taken to obviate changes in concentration on these accounts.

The principal points in favor of their use for calibrating purpose are the ready availability in pure form, wide range of viscosities, and ease of standardization as to glycerol content; C. P. glycerol of exceptionally high purity is available on the present market in concentrations from 95 to 99 per cent. The difference represents largely water, there being usually less than 0.01 per cent foreign impurities present in the c. P. grade. Consequently, the range of viscosities obtainable upon the more highly concentrated grade and its aqueous solutions is from 12.00 to 0.01 poises. By means of an accurate specific gravity determination the percentage glycerol concentration can be determined within ±0.02 per cent. With this information at hand, a table showing the absolute viscosities of varying concentrations would complete the information necessary for the purpose.

The literature contains several references to the viscosity of glycerol; the data of Archbutt and Deeley (1) and of Herz and Wegner (8) are perhaps the most widely quoted and used. The former authors worked with an instrument of their own design and determined absolute values for viscosities at 20° C. for eight concentrations of glycerol from approximately 40 to 97 per cent. These, together with their value for water, were used in constructing a table of viscosities corresponding to specific gravities from 1.000 to 1.260 at 20°/20° C.

While the data of these authors no doubt represent the best at present available, they are of questionable value for accurate calibrating purposes, principally because of the fact that only eight points of the viscosity curve were determined, thus necessitating interpolation between widely separated points. Moreover, the purity of the original glycerol which was purchased in 1896 would be open to question, since methods of glycerol manufacture at that time were quite crude when compared with present-day equipment and processes.

The purpose of this paper was to determine accurately the concentration-viscosity curve of solutions of commercial c. P. glycerol of highest purity over a limited room-temperature range—namely, 20° to 30° C.—and to show a comparison with the published values. A secondary purpose of the investigation was to determine sufficient data in the higher concentration range to make possible the accurate evaluation of the percentage glycerol concentration from the viscosity value. As a matter of fact, the choice of temperatures noted in the table of viscosities was made for the purpose of constructing an accurate temperature-correction table by means of which it would be possible to correct viscosity values made at any temperature between 20° and 30°C. to the nearest determined curve, and to read off directly the corresponding glycerol concentration. Such a table would be of considerable practical value in glycerol manufacture, since concentrations of 93 to 99.5 per cent are those most often dealt with in the glycerol refinery. The viscosity in this range changes very rapidly with concentration, and preliminary tests have indicated that evaluation by such a method is quite as practical, somewhat shorter, and quite as accurate as the usual specific gravity determination for evaluating glycerol concentration.

Brief mention should be made of the work of other authors on the subject. Herz and Wegner (8) made use of four Ostwald viscometers and constructed a temperature-concentration-viscosity table from 10 to 92 per cent glycerol at temperatures from 10° to 80° C. Their results are given in absolute units and are based on their own density table for glycerol concentration (7).

Kellner (10) determined the relative viscosities of glycerol solutions prepared from a "fermentation" glycerol by distillation, from 75 to 100 per cent glycerol (basis Gerlach specific gravity table, 15°/15° C.). He used the Engler viscometer at 24° C, and expressed his results in Engler units compared to water at the same temperature. He pointed out the possibility of the viscosity being used as a quality control in glycerol production and also as an index of its concentra-

Jones (9) in some studies of the falling ball method of viscosity measurement published some meager data on the viscosity of glycerol, but his figures should be considered only approximate, as they are not based on sufficiently accurate specific gravities.

Cocks (5) has compiled considerable data on this subject, supplementing these with many of his own determinations on a No. 1 Redwood viscometer, using the Higgins equation for calculating the absolute values. He extended the Herz and Wegner table up to 99.2 per cent glycerol and $100\,^\circ$ C. for the higher concentrations. Other authors on this subject include Müller (11), Schöttner (12), and Darke and Lewis (θ).

In this paper the glycerol viscosities of Archbutt and Deeley at 20° C. and those of Herz and Wegner at 20° and 30° C. will be compared with the present author's interpolated values at the same temperatures. The specific gravity data of each have been interpolated to percentage glycerol on the basis of the Bosart and Snoddy (4) apparent specific gravity-concentration tables at 20°/20° C. These comparisons are shown in Tables I and II.

Table I. Comparison of Data of Archbutt and Deeley with Those of Author

Sp. Gr.	Absolute Viscosities (20° C.) Archbutt and						
20°/20° C.)	GLYCEROL	Deeley	Author	VARIATION			
	%	Centipoises	Centipoises	%			
1,10136	40.00	3.72	3.75	+0.8			
1.1699	65.04	15.30	15.59	+1.8			
1.1848	70.45	23.60	23.90	+1.3			
1.2057	78.11	49.80	50.15	± 0.7			
1.2155	81.74	74.97	75.6	± 0.8			
1,2240	84.92	111.13	111.7	+0.5			
1,2463	93.32	407.90	408.8	+0.2			
1.2568	97.37	868.62	863.0	-0.7			
				Av. 0.85			

TABLE II. COMPARISON OF DATA OF HERZ AND WEGNER WITH THOSE OF AUTHOR

Sp. Gr.				Viscositie	s		
(20°/	GLYC-	Herz and	Wegner	Aut	thor	VARIA	TION
20° C.)	EROL	20° C.	30° C.	20° C.	30° C.	20° C.	30° C.
	%	Centi	poises	Cent	ipoises	%	%
1.0234	9.77	1.328	1.023	1.303	1.018	-1.9	-0.5
1.0487	19.96	1.844	1.406	1.767	1.358	- 4.4	-3.5
1.0741	29.77	2.516	1.891	2.480	1.862	-1.5	-1.6
1.1009	39.83	3.877	2.819	3.722	2.712	-4.2	-4.0
1.1288	50.12	5.922	4.161	6.090	4.270	+ 2.8	+2.6
1.1559	59.94	10.33	7.062	10.92	7.295	+ 5.4	+3.2
1.1835	69.98	24.24	15.17	22.86	14.30	-6.0	-6.1
1.2105	79.85	63.63	35.02	61.0	34.42	-4.3	-1.7
1.2237	84.81	99.56	53.61	110.4	58.7	+ 9.8	+8.7
1.2312	87.62	146.6	79.91	164.6	84.5	+10.9	+5.4
1.2357	89.30	195.3	99.09	211.2	105.2	+7.5	+5.8
1.2420	91.69	284. 4	149.5	312.6	149.5	+ 9.0	0.0

The original data of Archbutt and Deeley (fourth edition) contained values for only seven glycerol solutions, ranging from 40 to 97 per cent, which were prepared from "a pure glycerol purchased from Messrs. Hopkin and Williams in 1896." In the fifth edition, the values for one of these solutions were omitted, and data for two other solutions, prepared from "Hehner's c. p. Glycerol" purchased in 1922, were obtained.

It will be noted from Table I that the experimental values of Archbutt and Deeley are in close agreement with those of the author, for the most part within 1 per cent. However, in constructing their viscosity table they have interpolated and extrapolated their data over a range of specific gravities from 1.000 to 1.260 at 20°/20° C. by means of a graph of specific gravity vs. logarithm of viscosity. As pointed out previously, it was necessary for these authors in preparing their table to interpolate between widely separated points; and, whereas their determined values are close to the author's, many of their interpolated values are at variance with the author's as much as 3 per cent, indicating that their method of interpolation was in error. This is especially marked between their determined values for glycerol concentrations corresponding to 1.2240 and 1.2463 specific gravities. At these two points the variation from present values is 0.5 and 0.2 per cent, respectively, whereas their interpolated values between these two points are as much as 3.5 per cent higher than present figures. In this particular range the author's curve includes seven determined points. Also their highest determined value agrees with the author's within 0.7 per cent, whereas their extrapolated points above this figure widen this difference to 3.1 per cent at 1.260 specific gravity.

Table II, giving Herz and Wegner's and the corresponding values by the author, shows only fair agreement at all concentrations up to and including 50 per cent glycerol. At 85,

90, and 92 per cent the agreement is considered poor, the variation at 88 per cent and 20° C. being nearly 11 per cent. Although they did not record the specific gravities of the various solutions tested, it is assumed that they used their own density tables published previously (7) which we have converted to specific gravities at $20^{\circ}/20^{\circ}$ C.

GLYCEROL USED AND PREPARATION OF GLYCEROL-WATER SOLUTIONS

The material used in this investigation was a sample of c. P. glycerol which had been triple-distilled in vacuo in a commercial unit. In order to obtain as high a purity as possible, only the fraction condensing in the first receivers was used. The usual carbon bleaching operation was also omitted since even the best carbon blacks contain some inorganic salts which are leached out during the bleaching operation. The concentration of the sample as indicated by the apparent specific gravity at 25°/25° C. was 99.66 per cent (Bosart and Snoddy tables). When tested according to the U. S. P. and other special tests, the sample showed the following results:

	%
Carbonaceous and mineral residue	0.0070
Mineral residue (ash)	0.0016
Chlorides (Cl)	0.0005
Sulfates (SO ₄)	0.0005
Oxalates	Nil
Iron (Fe)	0.00004
Arsenic	Nil
Heavy metals	Nil
Fatty acids and esters	0.50 cc. 0.5 N NaOH

This glycerol was diluted with freshly boiled distilled water in making up a series of samples so that a range of concentrations from 0.00 to 99.66 per cent glycerol was covered in increments corresponding to appreciable changes in viscosities. Since the viscosity-concentration plot has the general form of a logarithmic curve, it is obvious that at the lower concentrations the increments could be chosen greater than at the higher concentrations without affecting the general accuracy of the curve to be drawn. Fifty-two sample solutions of one pint each were thus prepared and stored in one-pint glass bottles which were tightly stoppered. The complete neck of the bottle was then capped with paper to prevent dust from collecting on the lip and possible entrance to the contents when unstoppered.

No attempt was made to adjust these solutions to correspond to even percentages of glycerol, since this procedure is quite tedious and unnecessary when sufficient data for accurate interpolation are obtained.

SPECIFIC GRAVITY DETERMINATIONS

All specific gravities were determined in duplicate with a 50-cc. Geissler side-arm type pycnometer at 25°/25°C. This was filled with the sample which had previously been adjusted in the sample bottle to a temperature slightly lower than 25° C. so that expansion would occur during the period of conditioning in the pycnometer to 25° C. The filled pycnometer (without side-arm cap) was then placed in a water bath within 5 mm. of the lip, thus controlling the temperature of all the contents except that small amount contained in the side arm above the level of the water. The bath was then maintained at a temperature of $25^{\circ} \pm 0.05^{\circ}$ C. for a period of 25 minutes, at the end of which time the excess issuing from the capillary of the side arm was removed by blotting with a dry towel. The ground-glass cap was then placed on the side arm and the pycnometer dried with a towel, care being taken to remove any overflow glycerol adhering to the side arm with a damp cloth. The pycnometer was then weighed and the percentage of glycerol calculated on the basis of the Bosart and Snoddy glycerol tables (4) at this temperature.

The calibration of the pycnometer was previously made in

similar manner at the same temperature with freshly boiled distilled water. The values shown are, therefore, the apparent specific gravities (not corrected to vacuo) at 25°/25° C.

Calibration of Viscometers

Three viscometers were used of the type described by Bingham (3). The maximum fluidities obtainable with these particular instruments were 500, 7, and 3, and the instruments will be designated subsequently in this paper as 1, 2, and 3, respectively. The equation of viscosity for this type of instrument is

$$\eta = Cpt - \frac{C'\rho}{t}$$

where η = absolute viscosity

, absolute viscosity p= pressure, grams per sq. cm. $\rho=$ density t= time sec

= time, sec.

C, C' = constants of viscometer

The general method of calibration used was that described by Bingham (2). Viscometer 1 was calibrated, using water at 20°C. as the calibrating fluid (viscosity = 0.01005 poise). The absolute viscosity of a white mineral oil of the Nujol type was determined carefully on the same instrument, and this was used as the calibrating fluid in determining the constants of both viscometers 2 and 3.

Each determination was made at least in duplicate, and, as a further check on the calibration, each instrument was checked by a second suitable liquid the viscosity of which was known. Table III shows the liquids used and the values obtained.

TABLE III. VALUES OBTAINED WITH VARIOUS LIQUIDS

Liquid	V	ISCOMETER-	3	Viscosity
Diguin	*	~	•	Poise
Water, 20° C.	0.0100504			0.010050
Water, 25° C.	0.008912			0.008937
White mineral oil 1	0.41830	a	ª	0.41830^{a}
White mineral oil 2	0.1572	0.1569		0.1572
59.96% sucrose soln., 25° C.			0.4377	0.4375

a Calibrating liquid.

The calibration of viscometer 1 was checked with water at 25°C.; that of viscometer 2, with white mineral oil, the viscosity of which was determined on viscometer 1; that of viscometer 3, with a 59.96 per cent sucrose solution at 25° C. The viscosity of the last-named solution was taken from the published tables (3).

Table IV shows the constants of the three instruments as determined in the manner indicated above.

TABLE IV. CONSTANTS OF VISCOMETERS

CONSTANT	1	VISCOMETER 2	3
$_{C^{\prime}}^{C^{\prime}}$ $_{h_{1}}^{C}$	0.000,000,198,2	0.000,006,724,1	0.000,027,563
	0.017,84	0.017,86	0.017,82
	+0.24 cm. (right limb)	0.00 cm.	0.00 cm.

The temperature-control bath used in the viscosity determinations consisted of an inverted 3-gallon (11.4-liter) bottle with bottom removed. Each viscometer was securely clamped in a suitable frame so that it could be suspended in the water bath always in the same relative position.

The temperature control of the bath was entirely manual, although it was facilitated by the insertion of a coil of copper tubing, ³/₈-inch (0.95 cm.) in diameter and 8 feet (2.4 meters) long, through which either warm or cold water could be run from reservoir supplies located above the apparatus. In this way a control well within $\pm 0.05^{\circ}$ C. could be maintained. Special effort was made to control the temperature of the bath closer than this when making determinations on the higher concentrations of glycerol, the viscosities of which vary greatly with the temperature. Needless to say, all thermometers used in both the specific gravity and viscosity determinations were checked against a standard which had been calibrated at the Bureau of Standards.

Connections to the air pressure were made by means of short pieces of thick-walled gum-rubber tubing and three-way glass stopcocks. The pressure regulator was similar to the one described by Bingham except that the cylinders were of glass and permitted the attainment of varying pressures up to 200 cm. of water. Previous to admitting the air to this regulator, it was passed through a coarse regulator of the diaphragm type; also, in order to further stabilize the effective pressure, an empty 200-pound ammonia cylinder was connected to the system which served as a cushion against slight momentary fluctuations. A water manometer bent around two one-meter sticks placed end to end served to measure the pressure. The graduations of the meter sticks were checked against a standard steel tape. In general, all precautions noted by Bingham were observed in setting up the apparatus and in carrying out determinations.

VISCOSITY DETERMINATIONS

The detailed procedure of making the viscosity determination was as follows:

The glycerol sample was drawn up by means of a vacuum pump into a specially constructed pipet having a long small-bore delivery tube. The outside of this was then wiped to remove any adhering liquid, and the pipet inserted in the viscometer, bringing the tip down to the bulb. The transfer could usually

TABLE V. DATA ON PRESSURE AND TIME AT VARIOUS TEMPERATURES

Sp. Gr. (25°/	GLYC-	Vis		-At 20° C	Z.——	,	At 22.5°	C		-At 25° C	D.——		At 27.5°	C.—		-At <u>3</u> 0° (
25° C.)	EROL	TER		P	Time	p	P	Time	p	\boldsymbol{P}	$\mathbf{T}_{ ext{ime}}$	p	P	Time	p	P	Time
	%		•		Sec.			Sec.			Sec.			Sec.			Sec.
1.00913	3.85	1	140.05	139.49	401.2				139.96	139.24	355.4				139.86	138.97	318.6
1.01735	7.31	1	140.69	140.21	437.3				140.62	140.00	386.7				140.60	139.83	344.8
1.02516	10.58	1	188.38	187.66	357.9				188.27	187.35	315.6				188.22	187.05	280.6
1.03393	14.13	1	188.40	187.81	397.0				188.34	187.58	348.5				188.20	187.23	$\frac{309.2}{338.8}$
1.04197	17.40	1	188.46	187.97	438.5			• • •	188.32	187.68	383.8	• • •	• • •	• • •	188.27	187.46	330.0
1.04787	19.79	1	187.74	187.32	472.8				187.86	187.31	412.0				187.89	187.18	364.2
1.05744	23.55	i	188.66	188.33	534.4				188.60	188.16	464.2				188.63	188.06	407.8
1.06874	27.98	ī	188.51	188.26	622.6				188.49	188.16	538.0				188.43	188 00	470.0
1.07512	30.44	ī	188.53	188.32	681.8				188.49	188.21	586.8				188.38	188.01	511.8
1.08218	33.11	1	188.36	188.19	756.8				188.31	188.08	649.2			• • •	188.29	187.98	563.0
1.09054	36.29	1	188.30	188.17	859.4				188.28	188.10	735.4				188.24	188.00	634.6
1.09034	39.02	+	188.13	188.02	984.0		• • •		188.13	187.98	819.2				188.10	187.87	704.8
1.10468	41.60	1	188.09	188.00	1080.6				187.93	187.81	914.8				187.88	187.72	784.2
1.11322	44.78	Ť	187.99	187.93	1252.0				187.86	187.77	1054.4				187.87	187.75	899.0
1.12239	48.20	ī	187.61	187.56	1483.4				187.55	187.48	1240.4				187.58	187.49	1051.6
		-	201102	40,.00											104 00	104 00	1241.4
1.13084	51.33	1							185.00	184.95	1474.6			• • •	184.96	184.89 186.67	1415.2
1.13843	54.10	1		22122	2221-	. 2 * 2 -	-:':-	- i i ' .	44.14	62.30	366.0		• • •		186.72	150.07	
1.16698	64.50	2	85.24	85.19	261.7	85.15	85.09	233.4	85.17	85.10	209.0	89.17	89.08	181.0	89.17	89.06	163.7
1.16741	64.66	2	89.42	89.37	251.8	89.24	89.18	224.4	89.20	89.12 90.49	201.0 232.0	90.46	90.39	208.6	90.46	90.39	187.7
1.17369	66.94	2	90.61	90.57	293.7	90.59	90.54	260.5	90.55						90.14	90.09	239.8
1.18260	70.19	2												• • •	00.11	50.00	200.0

Sp. Gr. (25°/25° C.)

1.00000 1.00235 1.00475 1.00710

1.00950

Sp. Gr. (25°/

30° C.

0.800 0.817 0.836 0.856 0.877

Centipoises

0.893 0.912 0.935 0.959 0.984

be made in less than one minute, and the operator could judge the proper amount to be introduced reasonably close after a little practice. The overflow arrangement in the pipet was the final check on the absolute hydrostatic head used. Time was measured with a high-grade split-second stop-watch which was checked against a good pocket watch. For runs longer than 20 minutes, a high-grade pocket watch was used. All determinations were made in duplicate.

Inasmuch as Bingham has pointed out that there is some question as to the present method for calculating the magnitude of the kinetic energy correction, and has recommended publication of time and pressures, p and P, this has accordingly been done as shown in Table V. The values on viscometer 1 are for the left limb determination, and those on viscometer 2 are average pressures for duplicate determinations, there being no correction on this instrument for hydrostatic head. All values for $C'\rho/Ct^2 = 0.04$ cm. and lower have been omitted, since this is negligible in the resultant viscosity value. Obviously, the data given in this table will be of value only in the event of possible future information on the extent of the kinetic energy correction.

Table VI represents the actual data collected on all solutions. Table VII gives the interpolated values for each per cent of glycerol from 0 to 90 per cent, and for each 0.5 per cent from this point to 100 per cent, taken from carefully drawn graphs of the data over the full range.

TABLE VI. ACTUAL DATA ON ALL SOLUTIONS

GLYC- VISCOME-

---Viscosity-

25° C.)	GLYC- EROL %	VISCOM: TER	20° C.	22.5° C.	- Viscosity 25° C. -Centipoise	27.5° C.	30° C.	1.07925 1.08190 1.08455
1.00913 1.01735 1.02516 1.03393 1.04197	3.85 7.31 10.58 14.13 17.40	1 1 1 1	1.109 1.216 1.331 1.478 1.634		0.981 1.073 1.172 1.295 1.428		0.877 0.956 1.040 1.147 1.259	1.08715 1.08980 1.09245 1.09510 1.09775
1.04787 1.05744 1.06874 1.07512 1.08218	19.79 23.55 27.98 30.44 33.11	1 1 1 1	1.756 1.995 2.323 2.545 2.822		1.530 1.731 2.007 2.191 2.420		1.351 1.520 1.751 1.907 2.098	1.10040 1.10310 1.10575 1.10845
1.09054 1.09781 1.10468 1.11322 1.12239	36.29 39.02 41.60 44.78 48.20	1 1 1 1 1	3.207 3.595 4.029 4.668 5.518		2.741 3.054 3.407 3.927 4.611		2.364 2.625 2.919 3.347 3.909	1.11115 1.11380 1.11650 1.11915 1.12185
1.13084 1.13843 1.14251 1.14673 1.15115	51.33 54.10 55.59 57.12 58.74	1 1 1 1	6.516 7.600 8.282 9.092 10.070	7.494 8.209 9.074	5.409 6.266 6.804 7.447 8.184	6.203 6.776 7.430	4 552 5 236 5 679 6 187 6 770	1.12450 1.12720 1.12995 1.13265 1.13540
1.15389 1.15862 1.16147 1.16698 1.16698	59.74 61.46 62.50 64.50 64.50	1 1 1 1 2	10.787 12.061 14.99	9.679 10.793 11.642	8.756 9.731 10.473 11.96	7.918 8.792 9.438 10.79	7 222 7 986 8 548 9 750	1.13815 1.14090 1.14365 1.14640
1.16741 1.17369 1.18260 1.18863 1.19459	64.66 66.94 70.19 72.40 74.61	2 2 2 2 2	15.13 17.89 23.35 28.57 35.11	13.46 15.86 20.53 24.98 30.57	12.05 14.12 18.21 22.03 26.81	10.84 12.68 16.23 19.56 23.64	9.80 11.40 14.53 17.41 20.97	1.14915 1.15185 1.15460 1.15735 1.16010
1.19754 1.20302 1.20755 1.21145 1.21666	75.69 77.71 79.37 80.83 82.80	2 2 2 2 2	38.98 47.97 57.79 70.28 85.73	33.80 41.41 49.52 60.08 72.75	29.61 36.08 42.85 51.90 62.53	26.06 31.58 37.49 54.01	23.02 27.81 32.86 46.90	1.16285 1.16560 1.16835 1.17110
1.22061 1.22539 1.22670 1.23025 1.23557	84.27 86.07 86.56 87.89 89.89	2 2 2 2 2	103.17 131.08 140.42 172.2 231.6	87.23 110.20 117.87 143.4 191.5	74.50 93.52 99.86 120.9 160.6	64.08 79.81 85.20 102.7 135.1	55.29 68.64 73.12 87.65 114.5	1.17385 1.17660 1.17935 1.18210 1.18480
1.23799 1.24166 1.24333 1.24565 1.24731	90.81 92.19 92.82 93.70 94.32	2333333	268.0 337.9 375.6 442.3 481.7	220.5 276.5 306.8 359.9 390.7	183.8 229.2 254.7 295.9 321.5	154.4 191.6 212.1 245.6 266.3	130.4 161.0 177.9 205.9 222.3	1.18755 1.19025 1.19295 1.19565
1.24958 1.25077 1.25187 1.25288	95.19 95.65 96.08 96.48	3 3 3 3	565.6 618.5 671.6 724.0	457.6 499.5 542.1 582.9	374.9 408.3 441.8 474.8	309.7 336.6 363.6 389.9	257.2 279.6 300.6 322.4	1.19840 1.20110 1.20380 1.20655
1.25396 1.25701 1.25904 1.26113	96.89 98.06 98.84 99.66	3 3 3	783.5 986 1158 1385	629.6 789.8 926 1102	512.3 636.8 747.4 884	420.7 519.8 607.3 715.5	346.7 427.2 496.2 583.3	1.20923 1.21190 1.21455 1.21720 1.21990

TABLE VII. ABSOLUTE VISCOSITIES OF GLYCEROL SOLUTIONS (Interpolated)

22.5° C.

20° C.

GLYC-EROL

%

0.00(water) 1.005 1.00 1.029 2.00 1.055 3.00 1.083 4.00 1.112

1.01185 1.01425 1.01660 1.01900 1.02135	5.00 6.00 7.00 8.00 9.00	1.143 1.175 1.207 1.239 1.274		1.010 1.037 1.064 1.092 1.121		0.900 0.924 0.948 0.972 0.997
1.02370 1.02620 1.02865 1.03110 1.03360	10.00 11.00 12.00 13.00 14.00	1.311 1.350 1.390 1.431 1.473		1.153 1.186 1.221 1.256 1.292		1.024 1.052 1.082 1.112 1.143
1.03605 1.03850 1.04100 1.04345 1.04590	15.00 16.00 17.00 18.00 19.00	1.517 1.565 1.614 1.664 1.715		1.331 1.370 1.411 1.453 1.495		1.174 1.207 1.244 1.281 1.320
1.04840 1.05095 1.05350 1.05605 1.05860	20.00 21.00 22.00 23.00 24.00	1.769 1.829 1.892 1.957 2.025		1.542 1.592 1.644 1.699 1.754		1.360 1.403 1.447 1.494 1.541
1.06115 1.06370 1.06625 1.06880 1.07135	25.00 26.00 27.00 28.00 29.00	2.095 2.167 2.242 2.324 2.410		1.810 1.870 1.934 2.008 2.082		1.590 1.641 1.695 1.752 1.812
1.07395 1.07660 1.07925 1.08190 1.08455	30.00 31.00 32.00 33.00 34.00	2.501 2.597 2.700 2.809 2.921		2.157 2.235 2.318 2.407 2.502		1.876 1.942 2.012 2.088 2.167
1.08715 1.08980 1.09245 1.09510 1.09775	35.00 36.00 37.00 38.00 39.00	3.040 3.169 3.300 3.440 3.593		2.600 2.706 2.817 2.932 3.052		2.249 2.335 2.427 2.523 2.624
1.10040 1.10310 1.10575 1.10845 1.11115	40.00 41.00 42.00 43.00 44.00	3.750 3.917 4.106 4.307 4.509		3.181 3.319 3.466 3.624 3.787		2.731 2.845 2.966 3.094 3.231
1.11380 1.11650 1.11915 1.12185 1.12450	45.00 46.00 47.00 48.00 49.00	4.715 4.952 5.206 5.465 5.730		3.967 4.165 4.367 4.571 4.787		3.380 3.540 3.706 3.873 4.051
1.12720 1.12995 1.13265 1.13540 1.13815	50.00 51.00 52.00 53.00 54.00	6.050 6.396 6.764 7.158 7.562		5.041 5.319 5.597 5.910 6.230		4.247 4.467 4.709 4.957 5.210
1,14090 1,14365 1,14640 1,14915 1,15185	55.00 56.00 57.00 58.00 59.00	7.997 8.482 9.018 9.586 10.25	7.247 7.676 8.147 8.652 9.226	6.582 6.963 7.394 7.830 8.312	7.124 7.552	5.494 5.816 6.148 6.495 6.870
1.15460 1.15735 1.16010 1.16285 1.16560	60.00 61.00 62.00 63.00 64.00	10.96 11.71 12.52 13.43 14.42	9.83 10.54 11.26 12.04 12.90	8.823 9.428 10.11 10.83 11.57	8.015 8.544 9.107 9.73 10.38	7.312 7.740 8.260 8.812 9.386
1.16835 1.17110 1.17385 1.17660 1.17935	65.00 66.00 67.00 68.00 69.00	15.54 16.73 17.96 19.40 21.07	13.80 14.84 15.92 17.19 18.66	12.36 13.22 14.18 15.33 16.62	11.10 11.88 12.72 13.64 14.66	10.02 10.68 11.45 12.33 13.27
1.18210 1.18480 1.18755 1.19025 1.19295	70.00 71.00 72.00 73.00 74.00	22.94 25.17 27.56 30.21 33.04	20.23 21.97 24.01 26.41 28.96	17.96 19.53 21.29 23.28 25.46	15.96 17.38 18.89 20.53 22.34	14.32 15.56 16.88 18.34 19.93
1.19565 1.19840 1.20110 1.20380 1.20655	75.00 76.00 77.00 78.00 79.00	36.46 40.19 44.53 49.57 55.47	31.62 34.87 38.50 42.65 47.53	27.73 30.56 33.58 37.18 41.16	24.47 26.84 29.59 32.58 36.06	21.68 23.60 25.90 28.68 31.62
1.20925 1.21190 1.21455 1.21720 1.21990	80.00 81.00 82.00 83.00 84.00	62.0 69.3 77.9 87.9 99.6	52.77 58.74 66.1 74.5 84.3	45.86 51.02 56.90 64.2 72.2	40.00 44.15 49.30 55.10 62.0	34.92 38.56 42.92 47.90 53.63

TABLE VII. ABSOLUTE VISCOSITIES OF GLYCEROL SOLUTIONS TABLE VIII. DETERMINATION OF PERCENTAGE GLYCEROL BY (Interpolated) (Continued)

(IIIIII ODIIIDD) (Goittitaea)								
Sp. Gr.	GLYC-			Viscosity-				
(25°/25° C.)	EROL	20° C.	22.5° C.	25° C.	27.5° C.	30° C.		
	%			Centipoises				
1.22255	85.00	112.9	95.5	81.5	70.2	60.05		
1.22520	86.00	129.6	109.1	92.6	79.0	68.1		
1.22790	87.00	150.4	125.6	106.1	90.5	77.5		
1.23055	88.00	174.5	145.7	122.6	104.0	88.8		
1.23320	89.00	201.4	169.1	141.8	119.1	101.1		
1.23585	90.00	234.6	194.6	163.6	137.3	115.3		
1.23718	90.50	255.0	210.4	175.6	147.6	124.3		
1.23850	91.00	278.4	227.0	189.3	158.8	134.4		
1.23983	91.50	302.8	246.2	204.0	171.3	145.0		
1.24115	92.00	328.4	267.9	221.8	185.6	156.5		
1.24248	92.50	356.2	292.5	241.2	201.2	169.3		
1.24380	93.00	387.7	318.6	262.9	217.7	182.8		
1.24513	93.50	421.3	344.8	285.7	237.0	196.2		
$\frac{1.24645}{1.24778}$	$94.00 \\ 94.50$	$\frac{457.7}{498.5}$	374.0	308.7	255.8	212.0		
1.24110	94.00	495.5	406.0	335.6	278.2	229.0		
1.24910	95.00	545	443.8	366.0	301.8	248.8		
1.25038	95.50	601	495.0	397.8	327.5	271.4		
1.25165	96.00	661	532.0	435.0	357.6	296.7		
1.25295	96.50	731	584.0	476.8	391.5	324.3		
1.25425	97.00	805	645	5 22.9	428.4	354.0		
1.25555	97.50	885	713	571	470.0	387.4		
1.25685	98.00	974	784	629	514.4	424.0		
1.25815	98.50	1080	867	698	567	465.3		
$1.25945 \\ 1.26073$	99.00	1197	957	775	629	511.0		
1.26201	99.50 100.00	$1337 \\ 1499$	$\frac{1065}{1186}$	856	694	564		
1.40401	100.00	1499	1190	945	764	624		

Table VIII shows the comparison on a few lots of c. P. glycerol between percentage glycerol as determined by specific gravity and percentage as determined by viscosities at 20° and 25° C.

VARIOUS METHODS

	GL:	CEROL DETERMINATION	ons ———sac
Lor	By sp. gr. (25°/25° C.)	By viscosity (20° C.)	By viscosity (25° C.)
	%	%	%
1	94.86		94.86
$\frac{2}{3}$	94.94 94.96		$94.88 \\ 94.90$
4 5	94.87 94.94	94.93 95.01	94.75 94.95
<u>6</u>	94.97	94.98	94.94
7	94.94	94.98	94.92

LITERATURE CITED

- (1) Archbutt and Deeley, "Lubrication and Lubricants," 5th ed.,
- p. 193, C. Griffin & Co., London, 1927.
 (2) Bingham, "Fluidity and Plasticity," 1st ed., pp. 295-318, McGraw-Hill, 1922.
- Bingham and Jackson, Bur. Standards, Sci. Papers 298 (1917).
- Bosart and Snoddy, Ind. Eng. Chem., 19, 506 (1927).
- (5) Cocks, J. Soc. Chem. Ind., 48, 279 (1929).
 (6) Darke and Lewis, Ibid., 47, 1073 (1928).
- (7) Herz and Wegner, Z. deut. Ol- Fett-Ind., 45, 53 (1925).
- (8) Herz and Wegner, Ibid., 45, 401 (1925).
- (9) Jones, Phil. Mag., 37, 451 (1894).
- (10) Kellner, Z. deut. Ol- Fett-Ind., 40, 677 (1920).
- (11) Müller, Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, 133, IIa, 133 (1924).
- (12) Schöttner, Ibid., 77, 682 (1878); 79, 477 (1879).

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Composition of Crude Phosphoric Acid Prepared by Sulfuric Acid Process

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HOSPHORIC acid (H₃PO₄) is now produced in the United States by two processes-namely, the sulfuric acid process and the volatilization process. Data on the relative quantities of acid produced by these processes are not available, but it is known that a large portion of the acid used in the manufacture of chemicals for technical, industrial, and food purposes is produced by the volatilization process, whereas the greater portion of the

acid used in the manufacture of fertilizer salts, such as double or triple superphosphate and the ammonium phosphates, is produced by the sulfuric acid process. Although bone was formerly an important raw material for the manufacture of phosphoric acid, the domestic production of acid is now derived almost entirely from phosphate rock.

As shown by Ross, Durgin, and Jones (17), the volatilization process possesses an advantage over the sulfuric acid process in that it produces directly an acid of comparatively high purity. This is one of the reasons why volatilized phosphoric acid has met with so much favor in the manufacture of technical and food-grade phosphates. The phosphoric acid used in the manufacture of fertilizer salts is produced principally by the sulfuric acid process and, after

Six samples of crude phosphoric acid prepared by the sulfuric acid process, including one sample each of dilute and concentrated acid obtained from Florida pebble, Idaho, and Tennessee brownrock phosphate, respectively, have been analyzed for the following constituents: phosphoric acid, total silica, aluminum, iron, calcium, magnesium, sodium, potassium, manganese, copper, zinc, lead, chromium, vanadium, molybdenum, arsenic trioxide, sulfur trioxide, fluorine, chlorine, bromine, iodine, and organic carbon.

concentrating to the desired strength, is used directly, usually without purification. Consequently, the fertilizer salts contain the greater portion of the impurities present in the phosphoric acid. The amount and nature of the impurities will depend upon the composition of the phosphate rock and of the sulfuric acid used in its treatment.

Certain of the impurities, if present in sufficient concentration, may affect, either adversely or favorably, the value

of the fertilizers in promoting plant growth (11, 18). In an investigation of the action of crude and c. p. phosphoric acids on metals, Kosting and Heins (9) have shown that impurities present in the crude acid accelerate the corrosion of certain metals and alloys, whereas they act as corrosion inhibitors in certain other cases. When phosphoric acid made by the sulfuric acid process is used in the manufacture of technical and food-grade chemicals, considerable trouble is sometimes encountered because of the difficulty in reducing the content of impurities to the desired limits, and also because of the effect of the impurities in producing undesirable colorations in the finished products.

Ross, Durgin, and Jones (17) report analyses of several samples of crude and commercially refined phosphoric acids