

naturally accompany an increase in electrical polarity, an occurrence which is suggested by the fact that the absorption of light causes the halides to be more soluble in water and better conductors of electricity.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## THE VISCOSITY OF LIQUIDS CONTAINING DISSOLVED GASES<sup>1</sup>

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The measurement of the viscosity of liquids containing dissolved gases has been almost entirely neglected. Poiseuille<sup>2</sup> measured the viscosities of a saturated solution of carbon dioxide and of solutions of hydrochloric and hydrobromic acids. Wolfgang Ostwald<sup>3</sup> found that saturated solutions of nitrogen, carbon dioxide and oxygen at 20° had viscosities of 57.18, 56.5 and 55.62, respectively, as compared with 56.2 for pure water, and concluded that these gases had no effect on the viscosity of water.

This investigation was undertaken to determine the influence of dissolved gases on the viscosity of certain liquids.

### Experimental Part

#### Purification of Materials

**Organic Solvents.**—The substances employed were purified and dried by the usual methods and finally fractionated, the main fractions boiling within a 0.1° interval, or less. The heptane was kindly given by Professor Edward Kremers,<sup>4</sup> who obtained it by distillation of the volatile oils obtained from the oleoresin of *Pinus Jeffreyi*. The distillate thus obtained was freed from resinous materials by saturating the cold solution with hydrogen chloride. After washing with water to remove the hydrogen chloride, sodium was added to remove the last traces of water.

**Gases.**—The chlorine was prepared from hydrochloric acid and manganese dioxide, washed with a solution of copper sulfate and dried with sulfuric acid. The hydrogen sulfide was prepared from sodium sulfide and purified by passage through water, a 20cm. tube containing iodine and a long calcium chloride tube. The sulfur dioxide was either prepared from sodium bisulfite or taken from a cylinder of the liquefied gas; it was dried and freed from dust particles before using.

#### Apparatus

**Viscometer.**—The viscometer used in this work was a modified Ostwald-Washburn instrument.<sup>5</sup> The Bingham viscometer<sup>6</sup> is probably

<sup>1</sup> The work included in this paper is from the thesis presented by John R. Lewis in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

<sup>2</sup> Poiseuille, *Ann. chim. phys.*, **21**, 76 (1847).

<sup>3</sup> Wo. Ostwald, *Zool. Jahrb. Biol.*, **18**, 12 (1903).

<sup>4</sup> Kremers, *J. Am. Pharm. Assoc.*, **9**, No. 11, 1 (1920).

the most accurate for ordinary work, but could not be used in this work for the following reasons: (1) liquids containing dissolved gases could not be placed in the viscometer in the usual manner, due to the tendency of the gases to escape from saturated solutions; (2) the working volume, namely, the amount of liquid placed in the viscometer for measurement, is too

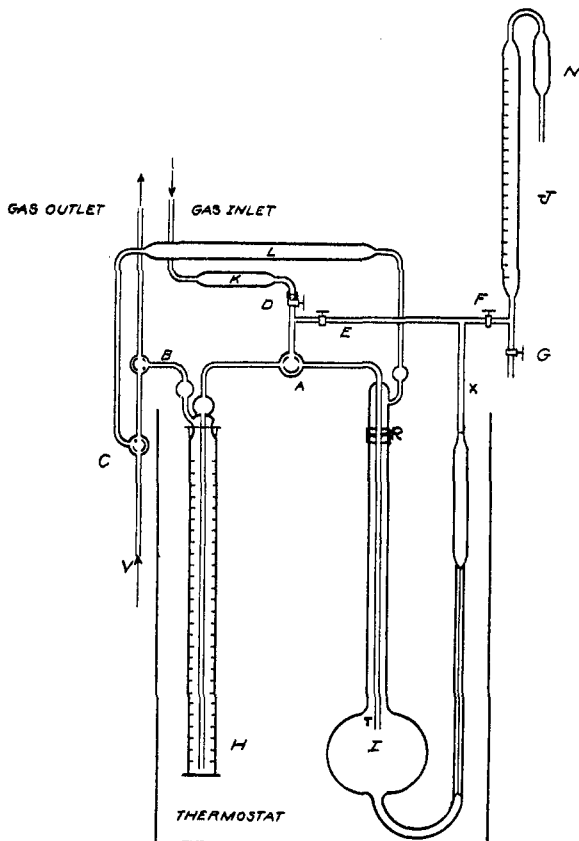


Fig. 1.—Apparatus used for viscosity determinations.

small, consequently the amount of liquid added from the saturating cylinder could not be measured accurately.

The viscometer used was made of glass and satisfied the dimensional requirements specified by Washburn and Williams. Quartz was not used because the liquids used have little or no solvent action on glass. The diameter of the tube above the lower bulb I (see Fig. 1) was much larger than that used by Washburn and Williams. This made it possible to insert

<sup>5</sup> Washburn and Williams, *THIS JOURNAL*, **35**, 739 (1913).

<sup>6</sup> Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., 1922, p. 76.

tube T through which liquids entered the viscometer from the saturating cylinder, without coming in contact with the rubber connection at R. The capacity of the bulb I was also greater than used by Washburn and Williams.

The filling of the above described viscometer was accomplished by means of the apparatus illustrated in Fig. 1.

This apparatus consisted of the graduated glass cylinder H, in which the liquids were saturated with the gas, after which the solutions were transferred to the viscometer by means of the tube through Stopcock A. A measured amount of liquid saturated in H could easily be transferred to the viscometer and liquid in the viscometer could also be forced back into the saturating cylinder if necessary. Gas entering the apparatus was dried and freed from dust particles by passing it through Tube K which contained fused calcium chloride and glass wool. Air used in forcing liquid from the viscometer to the cylinder, etc., was dried and freed from dust by passage through the tube L which also contained fused calcium chloride and glass wool. The whole apparatus was placed in a large thermostat the temperature of which was maintained at  $25^{\circ} \pm .02^{\circ}$ .

The pycnometer was of the Sprengel type with capillary stopcocks, and had a volume of 6 cc. Each pipet was also provided with a stopcock above the graduation mark. The titrating flask was an ordinary volumetric flask with an extra bulb sealed to the center of the bottom into which the solution to be analyzed was delivered, so that gas escaping from it would be absorbed in the supernatant layer of water in the flask. The stop watch, reading to 0.2 second, was checked against a United States Bureau of Standards watch.

Samples for determinations of density were obtained by attaching the pycnometer at D, Fig. 1, until it was completely filled; the top stopcock was then closed, the pressure relieved at C and then the bottom cock of the pycnometer was also closed. Finally D was closed. Three samples were drawn for each concentration and the average value used in calculating the density.

Samples for analysis were obtained in the same manner.

**Calibration of Viscometer.**—The viscometer constant was determined using 100 cc. of distilled water in the viscometer and the time of flow determined at  $25^{\circ}$  and also at  $0^{\circ}$ . The constant was calculated by means of the equation,  $K = \eta_0 / (t_0 \times D_0)$ , where  $K$  is a constant,  $\eta_0$  the viscosity of water at  $25^{\circ}$  or  $0^{\circ}$ ,  $t_0$  the time of flow in seconds,  $D_0$  the density of water at  $25^{\circ}$  or  $0^{\circ}$ . The results obtained are  $K_{25^{\circ}} = 310.3 \times 10^{-7}$ ;  $K_{0^{\circ}} = 310.9 \times 10^{-7}$ ;  $K_{av.} = 310.56 \times 10^{-7}$ . The values of  $K$  show that the viscometer obeyed Poiseuille's law accurately enough for these experiments.

It was necessary to find whether the volume of liquid forced into the viscometer from the reservoir H (Fig. 1) was always the same. This was determined by filling the viscometer several times and measuring the time of flow of each portion of the liquid forced over. The times of flow for

From the liter flask containing the sulfurous acid solution, 25cc. portions (or more or less as the case required) were removed, placed in a special 100cc. portions were 129.0, 128.8, 129.0, 129.2 and 128.8 seconds. To determine the change in time of flow with change in volume of liquid in the viscometer, the times of flow for different volumes of acetone and water were measured. The times of flow for 100 cc., 94 cc. and 87.5 cc. of water were 288, 287.5 and 286 seconds, respectively. For acetone, 120, 110, 100 and 90 cc. required 130.2, 129.5, 128.8 and 126.8 seconds, respectively. From the data given it is obvious that small errors in filling the viscometer may be neglected.

**Manipulations.**—Liquid was added to the cylinder H by disconnecting the tube K from D, and connecting D with a supply of the liquid. The liquid passed through the three-way stopcock A into H. When the liquid was to be saturated with gas before being forced into the viscometer, the gas used entered the apparatus through K, passing through D and A and escaping at the bottom of H. It rose through the liquid, the unabsorbed gas passing off through B. To transfer liquid from the cylinder into the viscometer, the three-way stopcock A was turned to connect H with I. Pressure was applied by way of B, forcing the liquid beyond A nearly to the right angle. A was then turned to shut off the supply of liquid from H and the volume in H recorded. A was again turned to connect H and I and gentle pressure applied to force the liquid into I. When the desired number of cubic centimeters had been forced into I, A was turned off and B opened to the air.

**Analysis of Solutions.**—Considerable trouble was encountered in finding a suitable method for the titration of sulfur dioxide in acetone solutions. The iodine method was impracticable because the acetone reacted immediately with the iodine. Acetone is not attacked by potassium permanganate in neutral solutions<sup>7</sup> and only slowly in acid solutions.<sup>8</sup> According to Lenher,<sup>9</sup> titrations of sulfurous acid solutions by permanganate are accurate to about 1%. In view of the fact that potassium permanganate attacks acetone very slowly in acid solutions, the permanganate titration method was adopted.

Ten (or more) cc. of the acetone sulfur dioxide solution was forced out of the viscometer bulb into a special pipet and then slowly into a volumetric flask previously nearly filled with water. After several minutes, the pipet was removed and water added to fill the flask to the graduation mark. This procedure diluted the solution and prevented the escape of gas except in solutions containing more than 25% of sulfur dioxide. Results for solutions of higher percentages of the gas were not concordant.

<sup>7</sup> *Jahresber. Fortschritte Chem.*, **1858**, 585.

<sup>8</sup> Denis, *Am. Chem. J.*, **38**, 572 (1907).

<sup>9</sup> Lenher, *THIS JOURNAL*, **35**, 733 (1913).

volumetric flask and titrated with standard potassium permanganate. The determinations checked well with one another and were also checked to 1% by a gravimetric method in which the sulfur dioxide was converted to sulfate and weighed as barium sulfate.

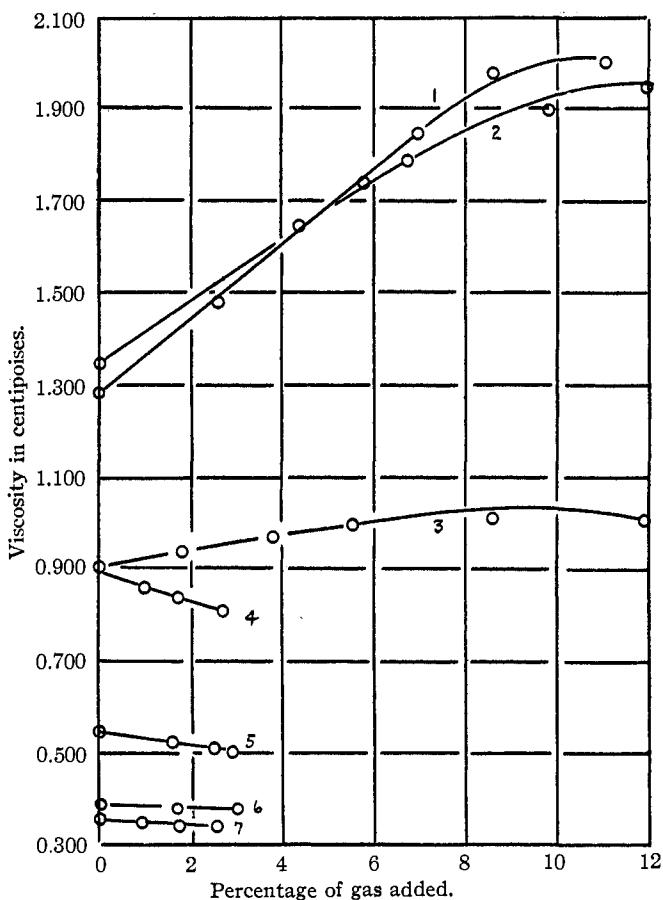


Fig. 2.—The viscosity of several solutions of gases in liquids. 1. Mixtures of water 75% and acetone 25% saturated with sulfur dioxide. 2. Mixtures of water 50% and acetone 50% saturated with sulfur dioxide. 3. Mixtures of water 25% and acetone 75% saturated with sulfur dioxide. 4. Carbon tetrachloride containing chlorine. 5. Chloroform and sulfur dioxide. 6. Heptane and sulfur dioxide. 7. Carbon disulfide and sulfur dioxide.

The amount of sulfur dioxide in the ether solutions was determined by titration with iodine, following the usual procedure. In all the other sulfur dioxide solutions, the permanganate method was used. The iodimetric

method was used in the analysis of the hydrogen sulfide and chlorine solutions.

**Calculations of Viscosities.**—The formula used for calculating the viscosity is that proposed by Ostwald. When the kinetic energy corrections are made, the formula can be written,  $\eta = \eta_0 \frac{D t}{D_0 t_0} - \frac{1.12 D V}{8 \pi l t}$ , where  $D$  is the density of liquid,  $t$  the time of flow of liquid,  $V$  the volume of flow,  $l$  the length of capillary, and  $\eta$  the viscosity of liquid.

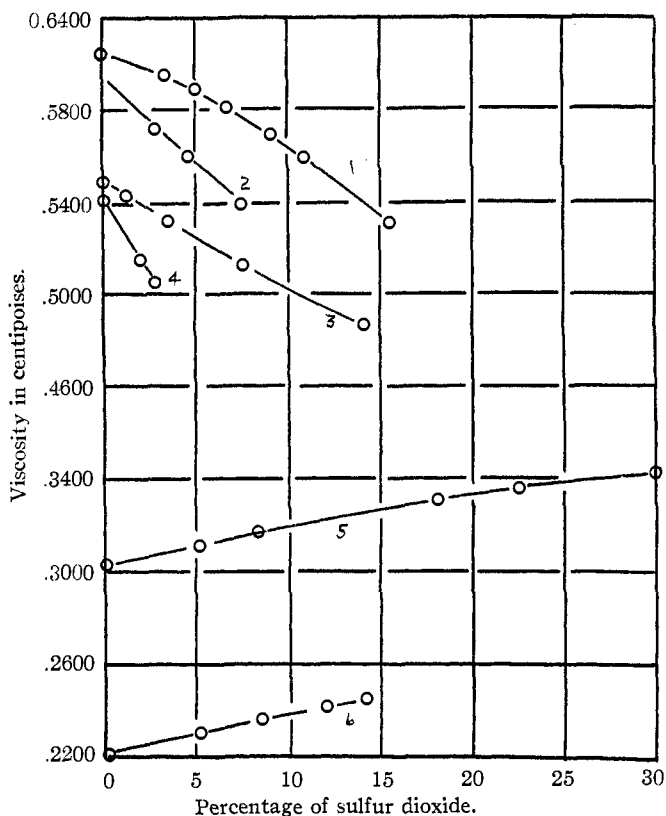


Fig. 3.—The viscosities of several sulfur dioxide solutions at 25°.

1. Xylene. 2. Benzene. 3. Toluene. 4. Chloroform. 5. Acetone.
6. Ether.

Using the methods described, viscosity measurements were made on several solutions. The data are given in Table I and shown graphically in Figs. 2 and 3. The values given cannot be considered reliable beyond the third decimal place in those cases where the concentration of gas was high, since the analytical method was accurate to only 0.5%. Also, the acetone-

TABLE I  
 VISCOSITY DATA (25°)

% of gas added	Density of solutions	Viscosity in centipoises	% of gas added	Density of solutions	Viscosity in centipoises
SULFUR DIOXIDE SOLUTIONS					
Carbon Tetrachloride			Toluene		
0.000	1.5830	0.8876	0.000	0.8602	0.5512
.328	1.5780	.8572	1.29	.8632	.5449
.685	1.5754	.8410	3.21	.8699	.5339
.780	1.5740	.8352	7.48	.8812	.5121
1.130	1.5732	.8200	14.00	.9088	.4881
Chloroform			Benzene		
0.000	1.4731	0.5422	0.00	0.8714	0.5961
1.88	1.4662	.5141	2.72	.8804	.5739
2.561	1.4650	.5053	4.52	.8872	.5629
2.90	1.4642	.5022	7.38	.8954	.5400
Ether			Xylene		
0.000	0.7084	0.2217	0.00	0.8590	0.6043
5.00	.7278	.2303	3.52	.8676	.5968
8.33	.7423	.2353	5.00	.8744	.5905
11.70	.7564	.2400	6.72	.8779	.5819
14.20	.7674	.2443	8.78	.8859	.5693
Carbon Disulfide			10.92	.8921	.5605
0.000	1.2512	0.3449	15.43	.9029	.5332
1.09	1.2497	.3404	A Mixture of Acetone and Water of Equal Parts by Volume		
1.825	1.2492	.3382	0.00	0.9291	1.3413
2.59	1.2490	.3369	4.37	.9708	1.6472
Heptane			6.71	.9877	1.7893
0.000	0.6766	0.3855	9.89	1.0136	1.8938
1.71	.6776	.3767	13.35	1.0307	1.9604
3.18	.6829	.3719	13.71	1.0310	1.9693
Chlorine in Carbon Tetrachloride			A Mixture of 75% of Acetone and 25% of Water by Volume		
0.00	1.5830	0.8876	0.00	0.8728	0.9016
1.08	1.5816	.8523	1.81	.8893	.9423
1.82	1.580	.8315	3.81	.8935	.9718
2.76	1.5793	.8013	5.56	.8998	.9980
Hydrogen Sulfide in Chloroform			8.58	.9204	1.0239
0.00	1.4731	0.5422	11.95	.9383	1.0469
.193	1.4697	.5257	17.63	.9644	1.0788
.287	1.4637	.5206	A Mixture of 25% of Acetone and 75% of Water by Volume		
Acetone			0.00	0.9684	1.2864
0.000	0.78502	0.3045	2.63	1.006	1.4766
5.340	.8050	.3122	5.86	1.0305	1.7328
18.02	.8570	.3313	6.97	1.0416	1.8419
22.22	.8761	.3365	8.83	1.0599	1.9850
26.52	.8972	.3415	11.03	1.0785	1.9861
30.62	.9130	.3430			
42.44	.9705	.3471			

water mixtures saturated with sulfur dioxide are not to be relied upon near saturation, since the gas added causes the acetone to separate from the water, forming a two-phase system.

### Discussion of Results

The results obtained with this viscometer show that the viscosities of liquids are changed by saturating with gases. From the data obtained, it appears that the change in viscosity depends on the solubility of the gas, the viscosity of the solvent, the viscosity of the gas (if it were liquid at the temperature at which the measurements are made), and the chemical nature of the solvent and solute.

### The Viscosity of Gaseous Solutions in Which the Concentrations of the Components Are Varied from Zero to One Hundred Per cent.

Due to the fact that the limited solubilities of the gases studied permit the establishment of but a small part of the curve except in the case of the curve for acetone and sulfur dioxide, it is impossible to classify these curves. To obtain additional information on the effect of a dissolved gas on the viscosity of a liquid, measurements were carried out over the whole range of concentration, namely, from 0 to 100% of each constituent.

### Apparatus

**Viscometer.**—The viscometer described above could not be used for the following reasons: (1) it could not withstand the pressure necessary to keep the sulfur dioxide liquid at 25°; (2) concentrated solutions could not be analyzed by the methods described above; (3) too much sulfur dioxide would be required for each series of operations.

The viscometer adopted was a modification of the Ostwald type, in which the two limbs just above the upper bulb F (Fig. 4) were connected. After the viscometer was filled with the desired liquid through tube *a*, this was sealed off, giving a closed system which would withstand the pressure. The ease of filling the bulb F depends on the dimensions of the tubing from which the viscometer is constructed. If the tube *x* were made of narrow tubing, for example, the liquid would not drain into the bulb F and fill it. Because of this fact, details of construction are given. Tubes *a*, *x*, and R were of 6 mm. inside diameter. Bulb F was of 4.6 cc. capacity, while the lower bulb was about 10 cc. The capillary tube was 8 cm. long, the total length from *u* to *x* being 24.5 cm. At the graduation mark M, the tubing was constricted until its internal diameter was 2 mm. This type of viscometer is unsuitable for liquids appreciably more viscous than water.

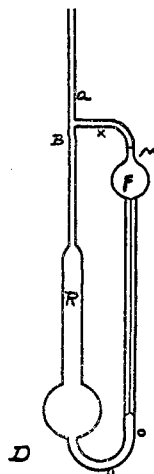


Fig. 4.—Closed type viscometer.



**Pycnometer.**—The pycnometer used in the experiments described above could not be used for high concentrations of sulfur dioxide at room temperatures. An instrument similar to that described by Bingham<sup>10</sup> was finally adopted. This pycnometer is an elongated bulb having a long neck closed by a ground-glass stopper. The instrument used in this work was of the same type; after each filling, the neck was closed by sealing it in the blast lamp, thus eliminating the use of a stopper and consequent danger of loss of gas. The volume of the liquid used, which was read on the graduated neck of the flask, was about 11 cc.

### Procedure

**Filling the Viscometer.**—This consisted of two operations: first, the addition of the liquid to be used, acetone for example; second, the addition

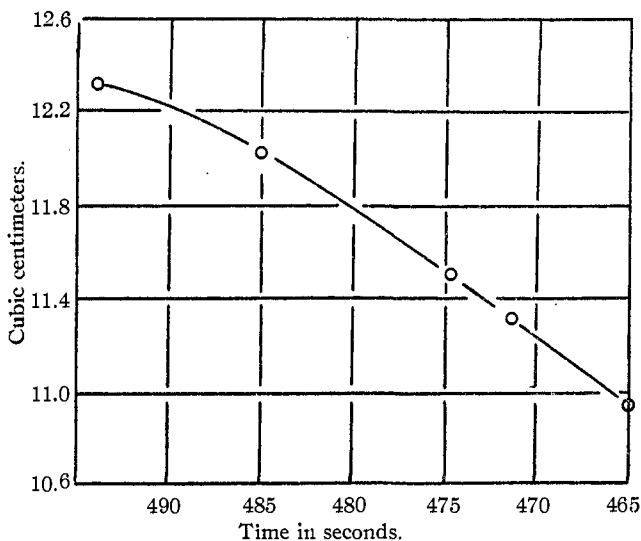


Fig. 5.—Water calibration curve for sealed viscometer (25°).

of the sulfur dioxide, which was the only gas used in these measurements. The clean, empty viscometer was weighed accurately, the liquid added by means of a capillary pipet, and the viscometer weighed again. It was then transferred to a Dewar flask containing a freezing mixture, and sulfur dioxide from a special container added. The viscometer was then closed by sealing the tube *a*. After coming to room temperature the filled viscometer plus the tubing drawn off at the blast lamp was weighed. This gave the weight of the solution. The viscometer was then placed in the thermostat in a suitable holder and allowed to come to the temperature of the bath. To measure the viscosity, the viscometer was inverted, allowing liquid to rise in the bulb *F* until it was completely filled. The visco-

<sup>10</sup> Ref. 6, p. 308.

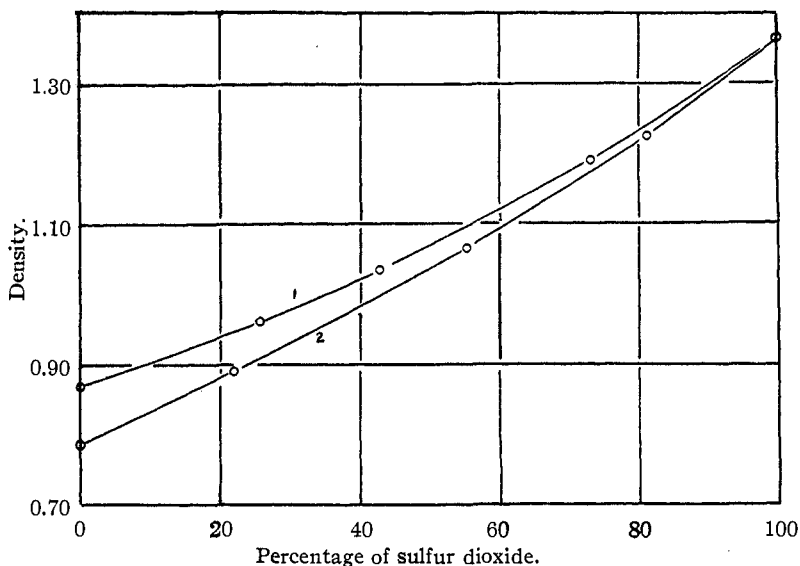


Fig. 6.—The densities of sulfur dioxide solutions. 1. Benzene. 2. Methyl alcohol.

meter was then placed right side up again, care being taken that the space *o-u* was completely filled with liquid, and the time required for the liquid to flow through the bulb F was measured in the usual manner.

**Calibration of Viscometer.**—Since it was impossible to place the

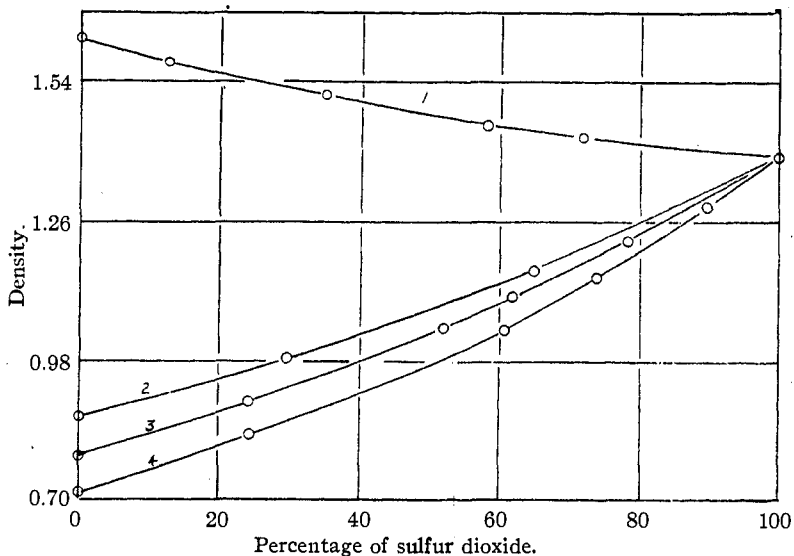


Fig. 7.—The densities of sulfur dioxide solutions: 1. Carbon tetrachloride. 2. Toluene. 3. Acetone. 4. Ether.

same amount of liquid in the viscometer for each experiment, it was necessary to calibrate the instrument, using different amounts of distilled water and determining the time of flow for each known volume. By plotting times of flow against volumes, a curve was obtained from which the necessary constant could be calculated for each run. It was found that 12.33, 11.514, 11.336, 12.032 and 10.920 cc. transpired in 494, 474.6, 472, 485.0 and 464.6 seconds, respectively. These data are shown graphically in Fig. 5.

**Density Determinations.**—Density determinations were made with solutions of widely differing concentrations, and the resulting values plotted on graph paper. From these curves the density of any solution could be obtained. The data are given in Table II and shown graphically in Figs. 6 and 7.

TABLE II  
THE DENSITY OF CERTAIN ORGANIC LIQUIDS CONTAINING SULFUR DIOXIDE

ACETONE						
% by wt. of SO <sub>2</sub> .....	0.00	24.74	52.42	62.07	78.45	91.35
Density.....	.7850	0.8885	1.0313	1.0886	1.1994	1.2950
ETHER						
% by wt. of SO <sub>2</sub> .....	0.00	24.94	61.17	74.41	90.17	
Density.....	.7084	0.8249	1.0308	1.1340	1.2661	
TOLUENE						
% by wt. of SO <sub>2</sub> .....	0.00	29.54	52.66	65.00	100.00	
Density.....	.8602	0.9721	1.0858	1.1422	1.3667	
BENZENE						
% by wt. of SO <sub>2</sub> .....	0.00	25.83	42.82	48.33	73.21	
Density.....	.8714	0.9627	1.0351	1.0747	1.1889	
CARBON TETRACHLORIDE						
% by wt. of SO <sub>2</sub> .....	0.00	2.47	8.72	12.52	35.54	48.15
Density.....	1.5830	1.5743	1.5490	1.5367	1.4720	1.4491
METHYL ALCOHOL						
% by wt. of SO <sub>2</sub> .....		0.00	21.58	55.32	81.25	
Density.....		0.7872	0.8814	1.0655	1.2261	

The values obtained with this viscometer for the pure liquids check well with values obtained by others; however, in certain cases values given here

TABLE III  
VISCOSITY DATA (25°)  
For 100% liquid SO<sub>2</sub>: d., 1.3667; vis., 0.2559 centipoise

ACETONE						
% of SO <sub>2</sub> .....	0.00	30.60	52.17	55.10	79.20	87.68
D. of soln.....	.78502	0.9129	1.0132	1.0410	1.2052	1.2690
Vis., centipoises.....	.3040	.3430	0.3410	0.3404	0.3016	0.2840

TABLE III (Concluded)

ETHER								
% of SO <sub>2</sub> .....	0.00	33.53	36.29	43.00	49.44	69.54		
D. of soln.....	.7084	0.8645	0.8796	0.9167	0.9590	1.0950		
Vis., centipoises.....	.2231	.2753	.2759	.2804	.2880	0.2876		
BENZENE								
% of SO <sub>2</sub> .....	0.00	19.24	47.42	49.56	73.61			
D. of soln.....	.8714	0.9370	1.0570	1.0672	1.1914			
Vis., centipoises.....	.5943	.4908	0.3798	0.3765	0.3032			
TOLUENE								
% of SO <sub>2</sub> .....	0.00	25.28	27.24	28.04	47.08	48.00	72.05	78.57
D. of soln.....	.8602	0.9527	0.9592	0.9622	1.0477	1.0527	1.1827	1.1872
Vis., centipoises	.5512	.4637	.4598	.4558	0.3905	0.3896	0.3107	0.3060
CARBON TETRACHLORIDE								
% of SO <sub>2</sub> .....	0.00	7.89	14.99	26.72	31.07	51.40	64.21	73.58
D. of soln.....	1.5830	1.5532	1.5276	1.4931	1.4819	1.4435	1.4183	1.4035
Vis., centipoises.	0.8876	0.6695	0.5587	0.4484	0.4168	0.3278	0.2987	0.2837
METHYL ALCOHOL								
% of SO <sub>2</sub> .....	0.00	8.02	25.53	31.236	48.73			
D. of soln.....	.7872	0.8180	0.8975	0.9300	1.0280			
Vis., centipoises.....	.5457	.5422	.5295	.5215	0.4641			
% of SO <sub>2</sub> .....	59.11	70.71	74.90	79.73	81.84			
D. of soln.....	1.0891	1.1602	1.1881	1.2242	1.2320			
Vis., centipoises.....	0.4178	0.3558	0.3433	0.3223	0.3118			

are lower, due to the kinetic energy corrections which others have not made in all cases. Table III gives the data obtained and Figs. 8 and 9 show them graphically.

### Discussion of Results

The viscosity data obtained with the sealed viscometer have been plotted in Fig. 9 and also converted to fluidities presented in Fig. 8.

In ideal systems fluidities are additive, and consequently the values of mixtures can be calculated. A mixture of two non-polar liquids such as heptane and octane should approach *ideality* and the mixture law should be obeyed, that is, the fluidities should be additive. On the other hand because of molecular changes, such as the formation of compounds in solution, a mixture of two polar substances does not obey the law, and the curves obtained deviate considerably from a straight line. The materials used in this work, when arranged in the order of their increasing polarity, are as follows: benzene, carbon tetrachloride and toluene, usually classed<sup>11</sup> as non-polar; then sulfur dioxide, ether, acetone and methyl alcohol, usually classed as polar. Mixtures of sulfur dioxide with benzene, carbon tetrachloride and toluene should give curves that deviate only slightly from a

<sup>11</sup> Hildebrand, "Solubility," The Chemical Catalog Company, 1924, p. 88.

straight line, while mixtures of sulfur dioxide and ether, acetone and methyl alcohol should give curves that are considerably sagged.

Examination of Fig. 8 shows that such is the case. The benzene and carbon tetrachloride curves (the toluene curve is not plotted because it is practically coincident with the benzene curve) are not straight, but the deviation is only moderate, indicating that the molecular attraction be-

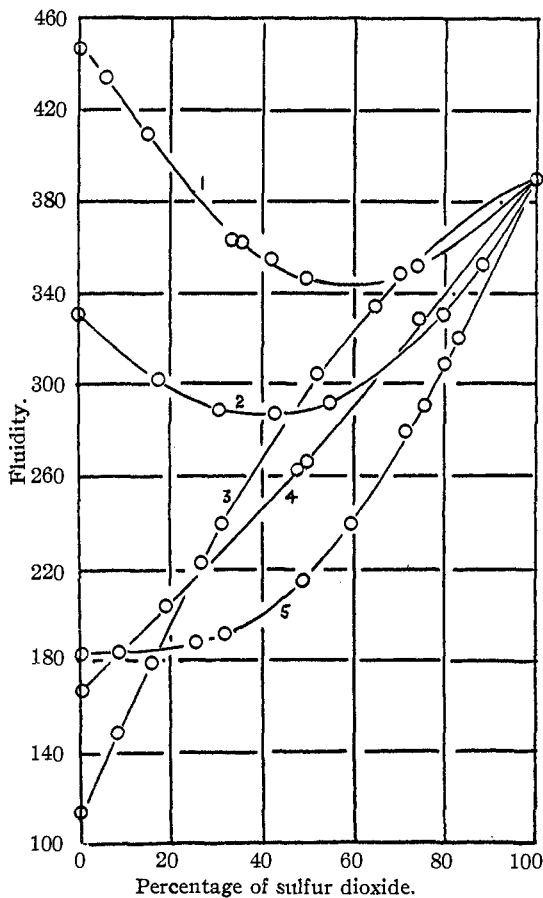


Fig. 8.—The fluidity curves for the systems shown in Fig. 9. 1. Ether. 2. Acetone. 3. Carbon tetrachloride. 4. Benzene. 5. Methyl alcohol.

tween the non-polar liquids and the moderately polar sulfur dioxide is not great. The ether, acetone and methyl alcohol curves are extremely sagged, showing that there has been molecular combination between these polar mixtures. The minima in the case of the acetone and ether curves are probably due to the formation of oxonium compounds.<sup>12</sup> The methyl alcohol

<sup>12</sup> THIS JOURNAL, 44, 1724 (1922).

curve deviates considerably from a straight line, indicating that here also there is molecular combination. If the fluidity value of pure methyl alcohol were near that of liquid sulfur dioxide at 25°, a minimum would doubtless be shown.

Examination of the viscosity curves (Fig. 9) shows in general the same phenomena. The ether and acetone curves pass through maxima. The

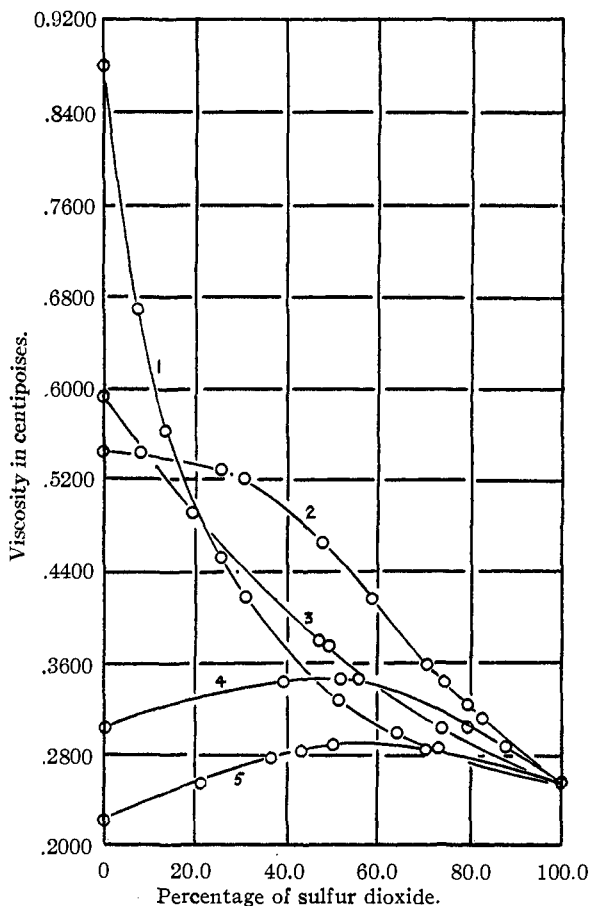


Fig. 9.—The viscosity of sulfur dioxide solutions. 1. Carbon tetrachloride. 2. Methyl alcohol. 3. Benzene. 4. Acetone. 5. Ether.

benzene and carbon tetrachloride curves are sagged, the sag in the carbon tetrachloride curve in this case being particularly noticeable. The methyl alcohol curve deviates considerably from a straight line. At higher concentrations of sulfur dioxide, the curve "bows" in the opposite direction from that shown at lower concentrations. Examination of the fluidity

curve of methyl alcohol (Fig. 8) shows no corresponding deviation at higher concentrations of sulfur dioxide, confirming Bingham's statement that viscosity curves are more sensitive indicators of molecular changes in solutions than are fluidity curves.<sup>13</sup>

In these experiments, liquid sulfur dioxide was used and curves were determined for various systems in which the concentration varied from 0 to 100% of each constituent. In the first experiments gaseous sulfur dioxide was dissolved in the various solvents under atmospheric pressure. For the same concentration of sulfur dioxide the viscosity values determined coincide with the values obtained using the sealed viscometer, thus furnishing evidence that a dissolved gas has the *properties of a liquid*.

Since the values obtained with the modified Washburn viscometer agree well with those obtained using the sealed viscometer for the same concentration of sulfur dioxide present, it is evident that the sealed viscometer used is as accurate as the modified Washburn instrument.

### Summary

1. A modified Washburn viscometer is described, which is suitable for determining the viscosity of liquids containing dissolved gases.

2. The viscosities of the following solutions were measured in concentrations varying from zero to saturation, at atmospheric pressure and 25°: sulfur dioxide with carbon tetrachloride, with acetone, with benzene, with toluene, with xylene, with ether, with heptane, with carbon disulfide, with chloroform, and with acetone-water mixtures; chlorine with carbon tetrachloride; hydrogen sulfide with chloroform.

3. A modified Ostwald viscometer is described, which can be used for viscosity determinations of solutions containing gases under pressure.

4. The viscosity and fluidity curves for the following systems have been determined, varying the concentration of the constituents from 0 to 100%: sulfur dioxide with acetone, with ether, with toluene, with benzene, with methyl alcohol, and with carbon tetrachloride.

5. The density curves for the same systems have been determined.

MADISON, WISCONSIN

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<sup>13</sup> Ref. 6, p. 83.