

A STUDY OF THE FLUIDITY RELATIONSHIPS IN THE SYSTEM, NITRIC ACID, SULFURIC ACID, AND WATER¹

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Introduction

The fluidity relationships existing in ternary mixtures have been the subject of few studies, although previous work of Bingham, White, Thomas, and Cadwell² indicates that such studies may give important evidence in regard to the formation of solvates. Ternary mixtures of nitric acid, sulfuric acid, and water are of particular interest because of their wide use in nitration, in connection with which there are important physico-chemical problems.

HISTORICAL INTRODUCTION

Nitric Acid

The physical properties of nitric acid have led many observers to the conclusion that it is hydrated in aqueous solution, and the existence of at least fifteen such hydrates has been reported in the literature. Of these only the mono- and tri-hydrates,³ both of which correspond to maximum points on the freezing point curve, have been isolated.

Hartley⁴ concluded that nitric acid of the specific gravity 1.490 was associated because of the pronounced difference in the absorption spectra of the same amounts of concentration and dilute acid. The work of Ramsay and Aston⁵ gave an association factor of 1.68 and 1.86 as measured from the

¹ Contributed from the Gayley Chemical and Metallurgical Laboratory of Lafayette College.

² Bingham, White, Thomas, and Cadwell: *Zeit. phys. Chem.*, **83**, 641 (1913).

³ Pickering: *Jour. Chem. Soc.*, **63**, 436 (1893).

⁴ Hartley: *Ibid.*, **133**, 663 (1903).

⁵ Ramsay and Aston: *Ibid.*, **65**, 167 (1894).

variation of surface energy for 99.8% acid at temperatures of 11.6°, 46.2°, and 78.2°.

Acid of ninety-five percent or over has irregular physical properties.¹ The contractions, conductivities, and to a slighter degree the refractive indices all show pronounced discontinuities at this concentration. This anomalous behavior, according to Veley and Manley,¹ indicates a decomposition into nitrogen pentoxide and water, rather than association. In this connection Küster and Munch² state that absolute, colorless nitric acid shows signs of decomposition when heated above its melting point.

The transpiration times of aqueous solutions of nitric acid have been investigated by Graham³ who found that the mixture showing maximum transpiration time contained 70% HNO_3 . He used a capillary opening into a bath, and worked with a constant pressure of one atmosphere. Neither the method of preparation of his nitric acid nor the method of determining its purity was described. No precautions were taken against the absorption of water by the very hygroscopic absolute acid. His original values, which were given in sufficient detail to permit their recalculation into terms of absolute fluidity, together with the method of recalculation are given in Table IV.

Bousfield⁴ and Poiseuille⁵ found that at low temperatures and in dilute solutions nitric acid decreased the viscosity of water, producing the so-called "negative viscosity." This negative curvature disappeared on raising the temperature to 25°.

Chèneveau⁶ found that nitric acid-water mixtures of the composition $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ displayed a maximum of relative viscosity.

¹ Veley and Manley: *Proc. Roy. Soc.*, **69**, 86 (1901).

² Zeit. anorg. Chem., **43**, 350 (1907).

³ Graham: *Phil. Trans.*, **151**, 376 (1861).

⁴ Bousfield: *Jour. Chem. Soc.*, **107**, 1787 (1915).

⁵ Poiseuille: *Ann. Chim. Phys.*, **21**, 76 (1847).

⁶ Chèneveau: *Comptes rendus*, **155**, 154 (1912).

Reyher¹ working at 25° found no indications of negative curvature. This result agrees with that of Bousfield who found that the negative curvature had disappeared at 25°.

Sulfuric Acid

While the existence of a large number of hydrates of sulfuric acid has been surmised from the properties of its aqueous solution, only the mono-hydrate² and the tetra-hydrate³ have been definitely isolated.

The absolute acid fumes at temperatures above 30° due to a partial dissociation into sulfur trioxide and water.

The viscosities of aqueous solutions of sulfuric acid at 25° have been studied by Dunstan and Wilson.⁴ The corrected values⁵ are given in Table VIII. They found a maximum viscosity at $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and a minimum at $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.

Chèneveau found that a mixture of the composition $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ had a maximum relative viscosity.

Graham measured the transpiration times of mixtures of sulfuric acid and water. Unfortunately he saw no necessity at the time of giving the same amount of detail as in the case of nitric acid, so his results cannot be recalculated in terms of absolute values. The mixture displaying maximum transpiration time contained 17.5% H_2O , closely corresponding to the compound $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (18.36% H_2O).

Mixtures of Nitric and Sulfuric Acids

Saposchnikow⁶ found that for mixtures of ninety-nine percent nitric acid with absolute sulfuric acid the vapor pressure followed the law of Henry, being proportional to the

¹ Reyher: *Zeit. phys. Chem.*, **2**, 744 (1888).

² Roscoe and Schorlemmer: "Treatise on Chemistry," 5th Ed., Vol. I, p. 441.

³ Pickering: *Jour. Chem. Soc.*, **57**, 339 (1890).

⁴ Dunstan and Wilson: *Ibid.*, **91**, 85 (1907).

⁵ Dunstan: *Proc. Chem. Soc.*, **30**, 104 (1914).

⁶ Saposchnikow: *Zeit. phys. Chem.*, **49**, 697 (1904).

amount of nitric acid present over a wide range of concentration. This seemed to him to indicate the absence of solvation. When over seventy percent nitric acid was present in the mixtures, the vapor pressure fell below that calculated from Henry's law. This was ascribed to a decomposition of the nitric acid into nitrogen pentoxide and water. Further evidence of such dehydration of the nitric acid was obtained from the density curves which showed a maximum at about ninety percent sulfuric. The same conclusion was also supported by a study of the nitrogen content of the vapor phase, which in mixtures containing a large excess of sulfuric acid rose above 22.2 percent (the nitrogen content of nitric acid). The conductivity curve of the same mixtures showed that the effect of adding a small amount of the ninety-nine percent nitric to sulfuric acid was to raise the specific conductivity very rapidly and in a manner similar to that of a small addition of water.

Ternary Mixtures of Nitric Acid, Sulfuric Acid, and Water

Saposchnikow showed that the effect of adding sulfuric acid to nitric acids of the specific gravities 1.48¹ and 1.40² was to raise the vapor pressure until, with increasing concentration of sulfuric acid, a maximum of vapor pressure was reached. This he interpreted as due to the sulfuric acid attracting the water combined with the nitric acid and thereby increasing the concentration of free nitric acid molecules. The density curves of mixtures of the above acids with sulfuric acid displayed a maximum density around ninety percent sulfuric, ascribed, as before, to a partial dehydration of the nitric acid. When the sulfuric acid was present in large excess, the vapor phase for the mixture contained a larger amount of nitrogen than corresponded to absolute nitric acid.

Saposchnikow's conclusion, that sulfuric acid when added to a solution of nitric acid is hydrated and produces an increased concentration of free nitric acid molecules, was sup-

¹ Saposchnikow: *Zeit. phys. Chem.*, **51**, 609 (1905).

² Saposchnikow: *Ibid.*, **53**, 225 (1905).

ported by the work of Pascal and Garnier¹ on the distillation of such mixtures. On the other hand, Berl and Samtleben² in a similar study obtained fundamentally different boiling point and vapor composition curves and concluded that for ternary mixtures with over 32% water, there was no evidence of any water binding action of the sulfuric acid at the boiling point.

Experimental Details

Two viscometers of the variable pressure type described by Bingham³ were used, the one (No. 6) for all mixtures having a viscosity in excess of four centipoises, the other (No. 5) for those of lower viscosity. Two bottles containing phosphorus pentoxide were placed in the pressure lines so that only dry air could come in contact with the acid mixtures in the viscometer.

The specific gravities of the more fluid mixtures were measured in a pycnometer of the type described by Bingham, Van Klooster, and Kleinspehn.⁴ For the more viscous mixtures which could not be introduced into this instrument, a pycnometer of the Ostwald-Sprengel type was used.

The viscosities were calculated by use of the formula $\eta = CPt - C'\rho/t$, where C and C' are constants of the instrument, P is the corrected pressure, ρ the density of the liquid, and t the time.

The constant for viscometer No. 5 was determined as 1.473×10^{-7} by calibration with water distilled first over acid permanganate, and then over alkaline permanganate. The constant for viscometer No. 6 had been determined by Mr. Hyden, as 0.7954×10^{-5} , by measuring the time of flow of linseed oil in a viscometer previously calibrated with water,

¹ P. Pascal and Garnier: *Ann. Chim.*, **15**, 253 (1921). See *Chem. and Met.*, **27**, 1025 (1922) for an English translation by Dr. F. C. Zeisberg.

² E. Berl and Samtleben: *Zeit. angew. Chem.*, **35**, 206 (1922). See *Chem. and Met.*, **25**, 1103, 1145 (1921) for English translation by Dr. F. C. Zeisberg.

³ Bulletin 298, Bureau of Standards.

⁴ Bingham, Van Klooster, and Kleinspehn: *Jour. Phys. Chem.*, **24**, 1 (1920).

and then using this linseed oil as a calibrating fluid. His values were checked by calibration with aniline freshly distilled from metallic sodium.

PREPARATION OF MATERIALS

Nitric Acid

Nitric acid of less than seventy percent HNO_3 was prepared by distillation of Baker and Adamson purest nitric acid under diminished pressure, the receiver being cooled by ice. The distilling apparatus was constructed entirely of glass, and was made by sealing off the neck of one Pyrex distilling flask, and then connecting the side arm *A* (Figure 1) of this flask to the constricted neck of a similar Pyrex flask.

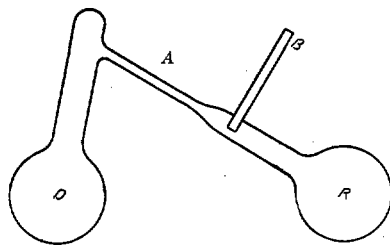


Fig. 1

Liquids were introduced at the side arm *B* and by tilting the apparatus were placed in the distilling end *D* without coming in contact with the receiving end *R*. Rejecting the first and second twenty-five cubic centimeters of distillate, served to wash out any few drops of the original liquid present in *R*. By elevating *R* the distillate was readily removed without contamination from any of the liquid in *D*. After introduction of the liquid into *D*, suction was applied at *B* by means of a water pump, the distilling end *D* placed in a water bath and *R* cooled by ice.

One distillation after rejecting the first and last fractions gave an acid of about 70% HNO_3 which contained from nil to 0.00002% nitrogen dioxide from nil to 0.000004% sulfuric acid, and from nil to 0.000003% hydrochloric acid.

For the concentrated nitric acid, Baker and Adamson's purest nitric acid was mixed with an equal weight of sulfuric acid and distilled in the above-described apparatus. The product obtained was mixed with an equal weight of sulfuric acid and then redistilled. The distillate after standing over

barium nitrate and silver nitrate was again distilled. The final product had a slight yellow tinge and became distinctly yellow on dilution with concentrated sulfuric acid. It analyzed 99.2% HNO_3 , 0.07% NO_2 with no traces of sulfuric or hydrochloric acid.

Sulfuric Acid

Sulfuric acid was prepared by distillation of Baker and Adamson's C. P. sulfuric acid. One distillation gave an acid

TABLE I
Fluidities of Mixtures of Nitric Acid and Water at 10°

Anal- ysis	% HNO_3 from Density	Mean	Vol. % HNO_3	Po gr/cm ²	P gr/cm ²	Time sec.	$\rho^{10/4}$	η centi- poises	ϕ abso- lute
99.24	100.00*	99.19	98.77	126.85	126.39	574.6	1.5306	1.0697	93.48
99.13	—	—	—	127.25	126.79	573.4	—	1.0709	93.38
88.32	88.68*	88.34	83.20	187.26	186.68	650.9	1.4958	1.7898	55.87
88.36	—	—	—	187.30	186.72	651.5	—	1.7918	55.81
—	—	—	—	187.68	187.10	649.4	—	1.7897	55.88
77.25	77.96*	77.24	68.92	198.04	197.71	854.0	1.4612	2.4870	40.21
77.23	—	—	—	198.47	198.14	853.0	—	2.4895	40.17
69.84	70.03	69.86	60.23	216.82	216.45	818.3	1.4275	2.609	38.33
69.89	69.60	—	—	217.22	216.89	817.3	—	2.611	38.30
62.61	—	62.66	52.30	216.70	216.36	830.6	—	2.647	37.78
62.60	—	—	—	217.08	216.76	828.1	—	2.644	37.82
52.10	52.19	52.13	41.57	216.96	216.57	749.2	1.3339	2.390	41.84
52.19	—	—	—	217.30	216.86	748.2	—	2.390	41.84
38.07	38.00	38.05	28.64	216.87	216.32	578.1	1.2427	1.842	54.29
38.01	—	—	—	217.19	216.47	578.0	—	1.843	54.23
25.28	25.31	25.28	18.10	216.85	216.03	471.4	1.1555	1.500	66.67
25.29	—	—	—	217.15	216.29	470.2	—	1.498	66.76
12.66	12.65	12.65	8.65	216.66	215.64	418.4	1.0739	1.329	75.24
12.63	—	—	—	216.94	215.90	417.9	—	1.329	75.24

The mean values in Column three are the mean of the analytical values, and of all the values obtained from the density determinations.

The values marked with an asterisk were not used in calculating the mean composition, because the densities observed were known to be too high due to the absorption of water by the acid in the pycnometer.

The volume percentages were calculated from the mean weight percent.

which contained about 98% sulfuric acid, 0.0001% iron, no trace of hydrochloric acid and 0.00011% lead sulfate.

The anhydrous sulfuric acid was made by dissolving sulfur trioxide fumes (obtained by heating oleum) in the pure sulfuric acid previously prepared. The excess of sulfuric acid anhydride was removed by dilution with sulfuric acid.

Analytical Methods

The compositions of the nitric acid-water mixtures were determined by titration with barium hydroxide solution, and then compared with the values obtained by interpolation from the density tables of Veley and Manley, and Lunge and Rey.¹ The mixtures of sulfuric acid and water were titrated with sodium hydroxide solution, and the values obtained compared with those interpolated from the density table of Domke.¹

TABLE II
Fluidities of Mixtures of Nitric Acid and Water at 20°

Anal- ysis	% HNO ₃ from	Mean	Vol. per- cent	Po gr/cm ²	P	Time sec.	$\rho^{20}/4$	η centi- poises	ϕ abso- lute
	Density								
99.24	100.00*	99.19	98.78	126.88	125.85	492.7	1.5108	0.9133	109.5
99.13	—	—	—	127.29	126.26	491.1	—	0.9133	109.5
88.32	88.79*	88.34	83.36	187.31	186.44	528.7	1.4793	1.4519	68.88
88.36	—	—	—	187.69	186.82	527.3	—	1.4510	68.92
77.25	77.93*	77.24	69.16	198.07	197.56	671.0	1.4451	1.9524	51.22
77.23	—	—	—	198.45	197.91	669.8	—	1.9626	51.21
69.84	69.94	69.86	60.51	216.84	216.23	640.2	1.4131	2.039	49.04
69.89	69.92	—	—	217.21	216.68	640.1	—	2.043	48.95
52.10	52.03	52.13	41.86	216.90	216.31	591.0	1.3222	1.883	53.11
52.19	—	—	—	217.24	216.56	590.0	—	1.882	53.13
38.07	38.14	38.05	28.88	217.17	216.31	473.6	1.2337	1.509	66.27
38.01	—	—	—	216.85	215.90	474.5	—	1.509	66.27
25.28	25.26	25.28	18.28	216.85	215.27	381.6	1.1492	1.210	82.64
25.29	—	—	—	217.15	215.61	381.0	—	1.210	82.64
12.66	—	12.65	8.74	216.64	215.11	333.6	1.0698	1.057	94.61
12.63	—	—	—	216.92	215.31	333.6	—	1.058	94.52
—	—	—	—	216.64	215.05	334.0	—	1.058	94.52

¹ Landolt and Börnstein's Tabellen, 3d edition.

The average of the values obtained by analysis, and from the density determinations, was taken as the composition of the mixture.

For the ternary mixtures, about one gram of the acid mixture was weighed in a sixty cm³ glass-stoppered flask, and titrated with sodium hydroxide using phenolphthalein as indicator. The sulfuric was estimated by precipitation with barium chloride on the same sample. The average of two determinations was taken as the composition.

Mixtures of Nitric Acid and Water

Tables I, II, and III give the experimental data for mixtures of nitric acid with water, the results being shown graphically in Figure 2. The mean values in Column three are

TABLE III
Fluidities of Mixtures of Nitric Acid and Water at 40°

Mean % HNO ₃	Vol. % HNO ₃	Po gr/cm ²	P gr/cm ²	Time sec.	$\rho^{40}/4$	η centipoises	φ absolute
99.19	98.80	126.93	125.22	378.6	—	0.6983	143.2
—	—	127.31	125.59	377.7	—	0.6987	143.1
88.34	83.56	187.31	185.62	375.0	1.4468	1.0253	97.53
—	—	187.69	185.98	374.2	—	1.0251	97.55
—	—	187.31	185.62	374.6	—	1.0242	97.64
77.24	69.48	198.21	197.06	452.0	—	1.3120	76.22
—	—	197.57	197.42	451.0	—	1.3115	76.25
69.86	60.86	216.80	215.59	427.0	1.3835	1.356	73.75
—	—	217.16	215.91	427.0	—	1.358	73.64
62.66	52.96	216.91	215.69	430.9	1.3480	1.369	73.05
—	—	217.27	216.01	430.9	—	1.371	72.94
52.13	42.22	216.87	215.57	405.0	1.2982	1.286	77.76
—	—	216.87	215.57	405.0	—	1.286	77.76
38.05	29.18	216.81	214.86	326.4	—	1.033	96.81
—	—	216.81	214.86	326.4	—	1.033	96.81
25.28	18.50	216.85	214.25	268.8	1.1355	0.8483	117.9
—	—	217.15	214.62	268.5	—	0.8488	117.8
12.65	8.86	216.65	213.36	230.4	1.0603	0.7241	138.1
—	—	216.93	213.63	229.8	—	0.7231	138.3

No values for the composition of the mixtures as calculated from the densities are given, due to lack of any tables for nitric acid-water mixtures at 40°.

the mean of the analytical results and of the composition as determined from the density at 10° and 20° C. For solutions above seventy percent nitric acid, only the analytical values were used to calculate the mean, as it was found that the densities measured in an Ostwald-Sprengler pycnometer were in error through the absorption of water by the acid in the pycnometer. This source of error was afterwards removed by suitable precautions.

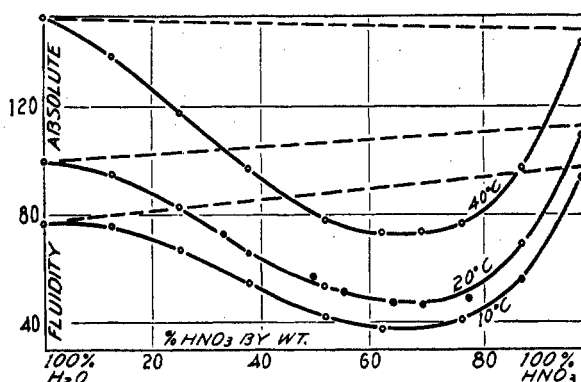


Fig. 2

Fluidity-Weight Concentration Curves for Aqueous Solutions of Nitric Acid

P_o is the observed pressure after making certain corrections,¹ P in Column six is the pressure used solely in overcoming viscous resistance,² ρ in column eight is the density, η is the viscosity in centipoises, and ϕ is the fluidity in absolute units.

The first addition of nitric acid to water depresses the fluidity only very slightly, a so-called "negative viscosity" effect, ascribed to a decomposition of the associated water molecules by the nitric acid.³ The effect of temperature which gradually eliminates the negative curvature is clearly

¹ Bulletin 278, Bureau of Standards.

² "Fluidity and Plasticity," p. 313.

³ Ibid., p. 184.

seen on comparing the curves for 10°, 20°, and 40° in Figure 2. The disappearance of the negative curvature with increase of temperature is probably due to the smaller association of water at high temperatures. The negative curvature is, as would be expected, more pronounced in very dilute solution, and both Poiseuille¹ and Bousfield² found that in dilute solutions of

TABLE IV

Graham's Data³ for Mixtures of Nitric Acid and Water at 20°

Volume of liquid transpired, $V = 8.075$ cc

Length of capillary, $L = 2.8$ cm

Radius of capillary = 0.00471 cm

Time of flow for water under one atmosphere pressure = 348.0 seconds.

By substituting the above values in the equations $C' = \frac{mV}{8l\pi}$ and

$C = \frac{\pi g r^4}{8Vl}$ the value of the constants can be obtained, as $C' = 0.1285$ and $C = 0.00002994/\text{Po}$.

The viscosity of a liquid = $CPoT - C'\rho/T$, or substituting the values obtained above = $0.00002994T - 0.1285\rho/T$

% HNO ₃	Time seconds	ρ	0.00002994T	$\frac{0.1258 \rho}{T}$	η centipoises	ϕ absolute
100.00	344.5	1.5046	1.0314	0.0561	0.9753	102.53
79.6	692.0	1.4358	2.0718	0.0267	2.0451	48.90
78.6	705.0	—	2.1108	0.0261	2.0847	47.97
76.9	712.0	—	2.1317	0.0258	2.1059	47.49
71.5	725.0	—	2.1707	0.0248	2.1459	46.60
70.0	732.0	—	2.1916	0.0245	2.1671	46.14
66.7	728.5	1.3816	2.1811	0.0244	2.1567	46.37
64.5	718.0	—	2.1497	0.0245	2.1252	47.05
63.6	712.0	—	2.1317	0.0246	2.1071	47.46
62.5	709.5	1.3598	2.1242	0.0246	2.1071	47.46
58.8	683.0	1.3407	2.0449	0.0252	2.0197	49.51
55.5	661.0	1.3239	1.9790	0.0257	1.9534	51.19
52.6	635.5	—	1.9027	0.0266	1.8761	53.30
50.0	593.0	1.2943	1.7754	0.0280	1.7474	57.23
33.3	472.0	—	1.4132	0.0339	1.3793	72.50

¹ Poiseuille: *Ann. Chim. Phys.*, **21**, 76 (1847).

² Bousfield: *Jour. Chem. Soc.*, **107**, 1781 (1915).

³ Graham: "Physical and Chemical Researches," *Phil. Trans.*, **153**, 373. (1861).

nitric acid the fluidity is raised above that of water. On further addition of acid the fluidity drops to a minimum value. The maximum deviation from a linear fluidity-volume concentration relationship¹ occurs for 40°, 20°, and 10° at 55.5%, 59.0%, and 60.0% nitric acid by volume, respectively, or at 65.0%, 68.5%, and 69.5% by weight. As the composition of the mixture showing maximum deviation from a linear fluidity-

TABLE V
Fluidities of Mixtures of Sulfuric Acid and Water at 10°

% H ₂ SO ₄ from		Mean	Vol. %	Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{10/4}$	η cp.	φ abs.
Analy- sis	Den- sity								
97.70	—	97.73	95.91	97.49	97.48	453.6	1.8472	35.17	2.843
97.77	—	—	—	97.13	97.10	454.7	—	35.12	2.847
87.62	87.92	87.76	79.63	75.67	75.66	650.4	1.8126	39.14	2.555
87.69	—	—	—	75.31	75.31	653.9	—	39.17	2.554
75.23	75.06	75.05	62.13	75.69	75.67	346.9	1.6796	20.88	4.789
74.83	—	—	—	75.35	75.32	348.2	—	20.86	4.794
62.67	62.65	62.67	47.80	66.22	66.13	165.0	1.5359	8.679	11.52
62.85	—	—	—	66.22	66.13	165.4	—	8.700	11.49
—	—	—	—	66.52	66.43	164.5	—	8.692	11.50
50.03	49.80	49.98	35.27	212.96	212.88	1561.1	1.4010	4.895	20.43
50.07	—	—	—	213.30	213.20	1558.1	—	4.893	20.44
37.86	37.79	37.81	24.90	199.10	198.95	1085.2	1.2911	3.180	31.45
37.80	—	—	—	199.14	199.28	1084.4	—	3.183	31.42
25.10	25.15	25.11	15.46	199.05	198.69	777.7	1.1860	2.276	43.94
25.05	—	—	—	199.35	198.99	776.5	—	2.276	43.94
11.76	11.69	11.72	6.75	199.43	198.98	615.5	1.0823	1.804	55.43
11.75	—	—	—	199.15	198.69	616.7	—	1.805	55.40
—	—	—	—	199.43	198.98	615.5	—	1.804	55.43

volume concentration curve shifts with the temperature, it cannot in this case be used to determine the presence of a hydrate. This, however, is to be expected in view of the negative curvature and of the fact that the acid forms at least two hydrates in aqueous solution.

Although the correction for kinetic energy in Graham's determinations amounts to about five percent, his values

¹ "Fluidity and Plasticity," p. 172.

given in Table IV and plotted as black dots in Figure 2, agree fairly with ours, except for the pure acid. But as he took no precaution against the absorption of water by his highly concentrated acid, his value for the absolute nitric acid, which is stated to be as hygroscopic as sulfuric acid, is probably too low.

TABLE VI
Fluidities of Mixtures of Sulfuric Acid and Water at 20°

% H ₂ SO ₄ from		Mean	Vol. %	Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{20}/4$	η cp.	ϕ abs.
Analy- sis	Den- sity								
97.70	—	97.73	95.91	97.48	97.47	312.4	1.8370	24.22	4.129
97.77	—	—	—	97.13	97.10	314.1	—	24.26	4.122
87.62	87.80	87.76	79.63	75.68	75.67	430.0	1.8008	25.88	3.864
87.69	—	—	—	75.32	75.31	432.2	—	25.89	3.863
75.23	75.06	75.05	62.13	75.70	75.67	246.4	1.6699	14.83	6.743
74.83	—	—	—	75.36	75.33	247.5	—	14.83	6.743
62.67	62.59	62.67	47.80	66.52	66.37	125.1	1.5265	6.604	15.14
62.85	—	—	—	66.22	66.07	126.1	—	6.627	15.09
—	—	—	—	66.52	66.37	125.4	—	6.620	15.10
—	—	—	—	66.22	66.07	125.8	—	6.611	15.13
50.03	50.00	49.98	35.27	212.95	212.80	1212.0	1.3951	3.779	26.32
50.07	—	—	—	213.29	213.12	1210.5	—	3.800	26.32
37.86	37.80	37.81	24.90	199.09	198.83	861.8	1.2837	2.524	39.62
37.80	—	—	—	199.43	199.12	860.9	—	2.525	39.60
25.10	25.14	25.11	15.46	198.98	198.40	598.5	1.1794	1.749	57.18
25.05	—	—	—	199.31	198.76	597.4	—	1.749	57.18
11.76	11.71	11.72	6.75	199.40	198.61	484.7	1.0782	1.418	70.52
11.75	—	—	—	199.12	198.39	484.9	—	1.417	70.57

Mixtures of Sulfuric Acid and Water

Figure 3 gives the fluidity-weight concentration curve for mixtures of sulfuric acid and water. The black dots in Figure 3 represent the data of Dunstan and Wilson for 25°, which are given in Table VIII. The data for our curves are given in Tables V, VI, and VII.

The first addition of sulfuric acid sharply depresses the fluidity, due probably to the formation of a viscous hydrate. The fluidity of the water, on addition of 11% H₂SO₄, is depressed

27%, 29%, and 32% at 10°, 20°, and 40°, respectively. On further addition of sulfuric acid the fluidity drops steadily until a concentration of about 85 percent acid is reached, when further addition of acid has little effect.

Dunstan and Wilson's observations at 25° display the same characteristics as our curves, and show the same rapid decrease in fluidity on the first addition of acid. Their curve has a

TABLE VII
Fluidities of Mixtures of Sulfuric Acid and Water at 40°

% H ₂ SO ₄ from		Mean	Vol. %	Po gr/cm ²	P gr/cm ²	Time sec.	$\rho^{40/4}$	η cp.	φ abs.
Analy- sis	Den- sity								
97.70	—	97.73	95.93	97.48	97.34	168.8	1.8170	13.07	7.651
97.77	—	—	—	97.12	97.00	169.4	—	13.07	7.651
87.62	87.75	87.76	79.71	75.67	75.62	219.8	1.7791	13.22	7.564
87.69	—	—	—	75.31	75.27	220.8	—	13.22	7.564
75.23	75.05	75.05	62.24	75.68	75.54	140.2	1.6509	8.424	11.87
74.83	—	—	—	75.34	75.20	140.7	—	8.416	11.88
62.67	62.61	62.67	47.92	54.29	54.04	98.4	1.5099	4.230	23.64
62.85	—	—	—	54.59	54.34	97.7	—	4.223	23.68
—	—	—	—	54.59	54.34	97.7	—	4.223	23.68
—	—	—	—	54.29	54.04	98.4	—	4.230	23.64
50.03	50.01	49.98	35.38	213.30	213.02	795.5	1.3796	2.496	40.06
50.07	—	—	—	212.94	212.66	796.5	—	2.495	40.08
37.86	37.81	37.81	24.99	199.06	198.37	564.7	1.2691	1.650	60.61
37.80	—	—	—	199.38	198.78	563.2	—	1.649	60.64
25.10	25.13	25.11	15.52	199.00	197.69	391.5	1.1663	1.140	87.72
25.05	—	—	—	199.30	197.97	390.6	—	1.139	87.80
11.76	11.71	11.72	6.78	199.36	197.65	332.5	1.0685	0.968	103.3
11.75	—	—	—	199.37	197.80	331.9	—	0.967	103.4

maximum at 93 percent of sulfuric acid by weight in a region where our observed values are too far apart to detect such a change.

Mixtures of Nitric Acid and Sulfuric Acid

Figure 4 shows the fluidity-weight concentration curves for mixtures of nitric acid and sulfuric acid, for 40°, 20°, and 10°. The experimental data are scattered throughout Tables X to

TABLE VIII

Data of Dunstan and Wilson for Aqueous Solutions of Sulfuric Acid
at 25°

% H ₂ SO ₄	ρ	η^* cp.	φ corrected ⁺
99.21	1.827	1.0616	4.05
97.51	1.832	0.85761	5.01
95.72	1.829	0.83255	5.17
93.41	1.823	0.84211	5.11
92.30	1.819	0.85088	5.05
91.36	1.815	0.87158	4.93
90.44	1.810	0.88508	4.86
89.57	1.805	0.95132	4.52
88.73	1.799	0.91588	4.70
88.00	1.795	0.92568	4.65
86.87	1.786	0.93366	4.61
86.98	1.787	0.93527	4.60
85.07	1.772	0.94794	4.54
84.97	1.770	0.92966	4.63
84.28	1.765	0.92529	4.63
83.98	1.761	0.91010	4.73
83.40	1.756	0.90866	4.73
82.58	1.747	0.89842	4.79
82.21	1.744	0.86571	4.97
81.54	1.737	0.83108	5.18
81.09	1.732	0.83452	5.15
80.24	1.723	0.78099	5.51
79.84	1.718	0.60272	7.14
79.53	1.715	0.74084	5.81
78.24	1.700	0.67228	6.40
76.27	1.677	0.57396	7.49
74.75	1.660	0.53603	8.02
70.52	1.610	0.40095	10.73
69.20	1.595	0.36450	11.80
67.21	1.572	0.32322	13.31
64.64	1.543	0.28042	15.34
58.36	1.475	0.20568	20.91
51.64	1.406	0.15370	27.98
49.86	1.388	0.14706	29.25
43.23	1.327	0.11293	38.09
36.43	1.267	0.09239	46.55
26.49	1.186	0.07119	60.42
15.70	1.104	0.05851	75.31
0.00	0.997	0.00891	112.2

* Dunstan and Wilson: Jour. Chem. Soc., 91, 85 (1907).

+ Dunstan and Wilson: Proc. Chem. Soc., 30, 104 (1914).

XII. Table IX gives the values obtained after allowing for the effect of the water present in the mixtures. The method of calculation is explained in the next section.

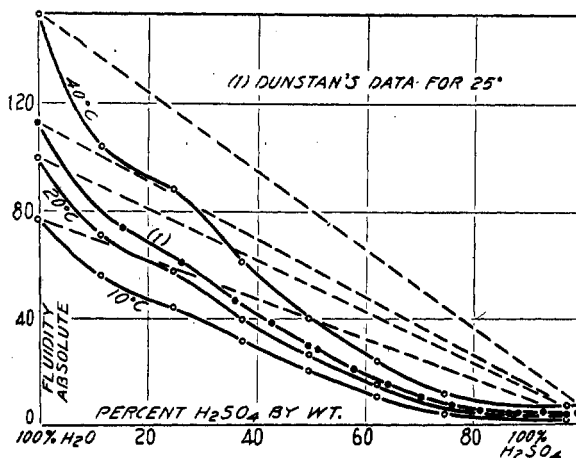


Fig. 3

Fluidity-Weight Concentration Curves for Aqueous Solutions of Sulfuric Acid

The first addition of nitric acid to the absolute sulfuric acid causes a slight decrease in fluidity, but the nitric acid has little effect on the fluidity until over 30 percent has been added,

TABLE IX
Fluidities of Mixtures of Sulfuric Acid and Nitric Acids

% HNO ₃	% H ₂ SO ₄	Volume percent HNO ₃	10° φ abs.	Volume percent HNO ₃	20° φ abs.	Volume percent HNO ₃	40° φ abs.
100.0	0.00	100.0	96.40	100.0	113.9	100.0	147.1
87.50	12.50	89.39	41.40	89.46	52.35	89.55	75.80
75.00	25.00	78.31	29.25	78.45	37.90	78.60	59.20
62.50	37.50	66.73	7.75	66.89	11.55	67.11	20.10
50.00	50.00	54.61	5.40	54.80	8.25	55.05	15.05
37.50	62.50	41.93	2.60	42.11	3.70	42.35	8.35
25.00	75.00	28.63	1.80	28.77	2.85	28.98	6.30
12.50	87.50	14.67	1.55	14.76	2.55	14.88	5.45
0.00	100.0	0.00	3.00	0.00	4.50	0.00	7.90

when further increases in the percentage of nitric acid rapidly increase the fluidity. In view of the wide difference in the fluidities of the components, the fact that the addition of 30

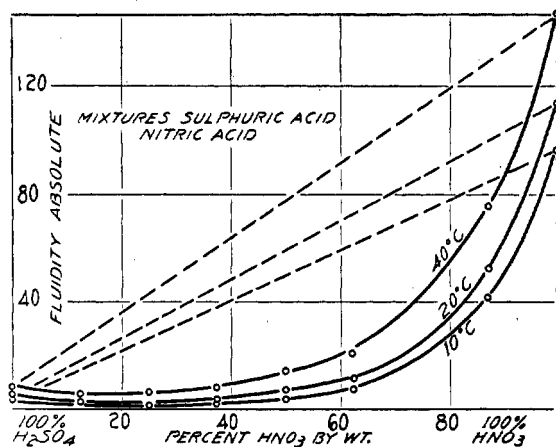


Fig. 4

Fluidity-Weight Concentration Curve for Mixtures of Nitric and Sulfuric Acids

TABLE X
Fluidities of Ternary Mixtures at 10°

% HNO ₃	% H ₂ SO ₄	Mean % HNO ₃	% H ₂ SO ₄	Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{10/4}$	η cp.	ϕ abs.
10.42	13.47	10.46	13.44	273.33	272.30	448.4	1.1623	1.7985	55.60
10.49	13.40	—	—	273.63	273.61	448.0	—	1.7989	55.59
12.58	—	12.56	21.41	273.52	272.97	607.6	1.2401	2.4430	40.93
12.53	21.41	—	—	273.52	272.99	607.2	—	2.4414	40.96
12.97	40.41	12.97	40.40	273.39	272.36	1207.4	1.4126	3.7437	20.58
12.97	40.40	—	—	273.75	273.53	1206.6	—	3.7446	20.57
12.62	—	12.61	48.64	272.99	272.92	1811.6	1.4910	7.2827	13.73
12.60	48.64	—	—	273.77	273.70	1804.4	—	7.2745	13.75
12.39	61.59	12.51	61.54	93.84	93.82	215.8	1.6365	16.098	6.212
12.62	61.48	—	—	93.52	93.46	216.2	—	16.073	6.222
11.96	73.00	11.93	73.04	101.98	101.96	371.7	1.7456	30.144	3.317
11.89	73.08	—	—	101.64	101.62	373.0	—	30.149	3.317
12.19	87.80	12.24	87.79	126.39	126.37	635.0	1.8931	6.383	1.567
12.18	87.78	—	—	126.06	126.00	635.9	—	6.373	1.569

TABLE XI
Fluidities of Ternary Mixtures at 20°

Mean % HNO ₃	% H ₂ SO ₄	Po	P	Time seconds	$\rho^{20}/4$	η cp.	ϕ abs.
10.46	13.44	273.30	271.75	351.8	1.1560	1.4082	71.01
—	—	273.60	272.06	351.6	—	1.4090	70.97
12.56	21.41	273.52	272.63	478.0	1.2326	1.9195	52.10
—	—	273.52	272.62	478.1	—	1.9199	52.09
12.97	40.40	273.38	273.11	930.6	1.4035	3.7437	26.71
—	—	273.74	273.47	929.6	—	3.7446	26.71
12.61	48.64	273.67	273.54	1363.7	1.4814	5.4946	18.20
—	—	273.29	273.16	1366.8	—	5.4994	18.18
12.51	61.54	74.91	74.84	194.2	—	11.560	8.650
—	—	74.59	74.52	195.2	—	11.570	8.643
11.93	73.04	101.72	101.67	246.7	1.7341	19.950	5.012
—	—	102.07	102.01	246.0	—	19.961	5.010
12.24	87.79	126.41	126.38	399.2	1.8778	40.13	2.492
—	—	126.03	126.00	400.1	—	40.10	2.494

TABLE XII
Fluidities of Ternary Mixtures at 40°

Mean % HNO ₃	% H ₂ SO ₄	Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{40}/4$	η cp.	ϕ abs.
10.46	13.44	273.25	269.98	240.7	1.1433	0.9572	104.47
—	—	273.60	270.32	240.0	—	0.9556	104.65
12.56	21.41	273.50	271.60	325.2	1.2179	1.3010	73.66
—	—	273.46	271.56	325.2	—	1.3008	73.88
12.97	40.40	273.40	272.77	604.9	1.3854	2.4304	41.15
—	—	273.76	273.13	604.0	—	2.4300	41.15
12.61	48.64	273.35	273.03	863.5	1.4628	3.4727	28.80
—	—	273.73	273.42	863.3	—	3.4768	28.76
12.51	61.54	74.59	74.39	113.6	1.6052	6.7219	14.88
—	—	74.91	74.72	113.0	—	6.7162	14.89
—	—	74.59	74.39	113.5	—	6.7159	14.89
11.93	73.04	69.71	69.63	184.9	—	10.241	9.765
—	—	69.38	69.28	186.0	—	10.250	9.756
12.24	87.79	126.39	126.32	189.5	1.8557	19.04	5.252
—	—	126.01	125.92	190.1	—	19.04	5.252

percent of nitric acid with its high fluidity to the highly viscous sulfuric acid has so little effect on the fluidity would seem to indicate some form of combination.

The maximum deviation of the fluidity-volume concentration curves from a linear relationship, which should¹ indicate

TABLE XIII
Fluidities of Ternary Mixtures at 10°

% HNO ₃	% H ₂ SO ₄	Mean		Po gr/cm ²	P gr/cm ²	Time sec.	$\rho^{10/4}$	η cp.	φ abs.
		% HNO ₃	% H ₂ SO ₄						
23.44	12.44	23.38	12.49	273.28	272.61	549.71	1.2430	2.207	45.30
23.32	12.54	—	—	273.28	270.15	555.02	1.2085	2.208	45.28
25.69	24.74	25.64	24.77	273.34	273.04	874.01	1.3644	3.515	28.45
25.58	24.80	—	—	273.70	273.46	873.4	—	3.518	28.42
24.44	36.80	24.40	36.80	273.36	273.24	1504.71	1.4653	6.056	16.51
24.35	36.80	—	—	273.73	273.61	1503.9	—	6.061	16.50
24.76	48.93	24.76	48.96	50.17	50.14	275.91	1.5851	11.003	9.088
24.77	48.99	—	—	49.85	49.74	278.1	—	11.002	9.089
—	—	—	—	50.17	50.14	275.6	—	10.991	9.098
—	—	—	—	49.86	49.83	278.1	—	11.022	9.073
24.10	61.08	24.04	61.14	76.25	76.23	330.31	1.7003	20.027	4.993
23.98	61.19	—	—	75.92	75.91	332.0	—	20.046	4.988
27.00	72.89	27.18	72.96	126.09	126.06	474.51	1.8513	47.58	2.102
27.35	73.03	—	—	125.71	125.69	475.3	—	47.52	2.104

TABLE XIV
Fluidities of Ternary Mixtures at 20°

Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{20/4}$	η cp.	φ abs.
% HNO ₃	% H ₂ SO ₄						
23.38	12.49	273.24	272.09	421.7	1.2348	1.6901	59.17
—	—	273.56	271.88	422.0	—	1.6900	59.17
25.64	24.77	273.32	272.83	682.0	1.3546	2.7408	36.49
—	—	273.68	273.19	681.1	—	2.7408	36.49
24.40	36.80	273.32	273.17	1137.0	1.4547	4.575	21.86
—	—	273.70	273.11	1134.1	—	4.579	21.84
—	—	273.32	273.76	1135.8	—	4.580	21.84
24.76	48.96	50.23	50.17	200.3	1.5738	7.993	12.51
—	—	49.91	49.85	201.8	—	8.001	12.50
—	—	50.25	50.19	200.6	—	8.008	12.49
24.04	61.14	59.12	59.09	293.0	1.6895	13.771	7.262
—	—	58.77	58.75	294.7	—	13.771	7.262
27.18	72.96	126.12	126.08	298.3	1.8382	29.916	3.343
—	—	125.74	125.74	298.9	—	29.886	3.346

¹ "Fluidity and Plasticity," p. 174.

the composition of any solvate present, occurs at volume concentrations corresponding to the weight concentrations of 68,

TABLE XV
Fluidities of Ternary Mixtures at 40°

Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{40/4}$	η cp.	ϕ abs.
% HNO ₃	% H ₂ SO ₄						
23.38	12.49	273.23	270.83	290.0	1.2184	1.1569	86.44
—	—	273.55	271.16	289.8	—	1.1575	86.39
25.64	24.77	273.30	272.22	451.4	1.3370	1.810	55.25
—	—	273.64	272.52	450.9	—	1.810	55.24
24.40	36.80	273.29	272.86	730.0	1.4337	2.934	34.08
—	—	273.67	273.24	729.5	—	2.936	34.06
24.76	48.96	50.34	50.15	120.0	1.5518	4.787	20.89
—	—	50.02	49.83	120.8	—	4.788	20.89
24.04	61.14	58.85	58.75	160.0	1.6666	7.4763	13.38
—	—	59.19	59.08	159.0	—	7.4725	13.38
—	—	58.85	58.75	160.0	—	7.4763	13.38
27.18	72.96	126.16	126.02	142.7	1.8147	14.304	6.99
—	—	125.78	125.63	143.0	—	14.290	6.998

TABLE XVI
Fluidities of Ternary Mixtures at 10°

% HNO ₃	% H ₂ SO ₄	Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{10/4}$	η cp.	ϕ abs.
		% HNO ₃	% H ₂ SO ₄						
38.92	12.11	38.77	12.20	273.30	272.87	713.8	1.3470	2.8690	34.86
38.63	12.29	—	—	273.64	273.21	712.6	—	2.8677	34.87
33.43	23.90	34.42	23.89	273.19	273.06	1020.7	1.4119	4.1054	24.36
33.41	23.89	—	—	273.54	273.41	1018.4	—	4.1014	24.38
35.21	38.44	35.21	38.44	51.80	51.74	198.1	1.5541	8.1522	12.27
35.21	38.42	—	—	51.64	51.64	198.6	—	8.1575	12.26
35.20	47.65	35.25	47.65	60.57	60.50	266.2	1.6535	12.81	7.806
35.30	—	—	—	60.23	60.18	267.2	—	12.79	7.819
37.15	62.80	37.17	62.79	97.59	97.55	417.8	1.8127	32.42	3.084
37.19	62.79	—	—	97.23	97.21	418.6	—	32.37	3.089

68, 68.5 percent for 40°, 20°, and 10°, respectively. This corresponds approximately to the compound 3HNO₃·H₂SO₄ which contains 65.9 percent nitric acid.

TABLE XVII
Fluidities of Ternary Mixtures at 20°

Mean		Po	P	Time	$\rho^{20}/4$	η	ϕ
% HNO ₃	% H ₂ SO ₄	gr/cm ²	gr/cm ²	seconds		cp.	abs.
38.77	12.20	273.28	272.59	560.9	1.3361	2.2521	40.40
—	—	273.62	272.92	559.8	—	2.2504	44.44
33.42	23.89	273.22	272.85	784.9	1.3995	3.1545	31.70
—	—	273.62	273.25	784.1	—	3.1559	31.69
35.21	38.44	52.02	51.88	145.6	1.5405	6.008	16.66
—	—	51.71	51.58	146.3	—	6.002	16.64
35.25	47.65	60.24	60.17	191.6	—	9.1697	10.91
—	—	60.56	60.49	190.6	—	9.1703	10.90
35.17	62.79	97.83	97.79	268.5	1.8010	20.885	4.788
—	—	97.47	97.43	268.3	—	20.870	4.792

TABLE XVIII
Fluidities of Ternary Mixtures at 40°

Mean		Po	P	Time	$\rho^{40}/4$	η	ϕ
% HNO ₃	% H ₂ SO ₄	gr/cm ²	gr/cm ²	seconds		cp.	abs.
38.77	12.20	273.24	271.69	375.8	—	1.5039	66.49
—	—	273.58	272.03	375.6	—	1.5050	66.45
33.42	23.89	273.28	272.41	510.7	1.3784	2.0492	48.80
—	—	273.63	272.79	509.6	—	2.0476	48.84
35.21	38.44	51.78	51.48	89.7	1.5168	3.6730	27.26
—	—	52.08	51.76	89.1	—	3.6680	27.23
35.25	47.65	60.56	60.35	110.2	1.6107	5.290	18.90
—	—	60.56	60.35	110.2	—	5.290	18.90
—	—	60.24	60.03	110.7	—	5.286	18.92
37.17	62.79	97.93	97.77	133.7	1.7750	10.398	9.618
—	—	97.55	97.39	134.2	—	10.396	9.619

Ternary Mixtures

Forty-five mixtures were prepared so as to contain as nearly as possible some multiple of 12.5 percent of each of the three components. Since the composition of the mixtures as determined by analysis always differed somewhat from the desired concentrations, the fluidity values for mixtures of the desired compositions were obtained by the following method.

TABLE XIX
Fluidities of Ternary Mixtures at 10°

% HNO ₃	% H ₂ SO ₄	Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{10/4}$	η cp.	ϕ abs.
		% HNO ₃	% H ₂ SO ₄						
50.29	12.31	50.26	12.31	273.34	273.03	868.8	1.4192	3.4940	28.62
50.24	12.31	—	—	273.67	273.36	867.3	—	3.4922	28.64
48.88	—	48.87	25.06	273.10	272.96	1326.4	1.5147	5.3330	18.75
48.86	25.06	—	—	273.53	273.39	1324.4	—	5.3333	18.75
50.90	36.90	50.93	36.90	44.31	44.25	206.4	—	7.2643	13.77
50.95	36.90	—	—	44.63	44.57	204.9	—	7.2637	13.77
47.10	52.63	47.16	52.60	78.82	78.79	332.3	—	20.826	4.802
47.22	52.56	—	—	79.18	79.15	331.1	—	20.846	4.797

Fluidities of Ternary Mixtures at 20°

% HNO ₃	% H ₂ SO ₄	Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{20/4}$	η cp.	ϕ abs.
		% HNO ₃	% H ₂ SO ₄						
50.26	12.31	—	—	273.33	272.82	670.4	1.4064	2.6940	37.12
—	—	—	—	273.64	273.13	669.7	—	2.6943	37.12
48.87	25.06	—	—	273.18	272.93	1000.2	1.5011	4.0210	24.87
—	—	—	—	273.58	273.33	998.6	—	4.0205	24.87
50.93	36.90	—	—	44.33	44.22	151.3	—	5.3214	18.79
—	—	—	—	44.33	44.22	151.6	—	5.3320	18.76
47.16	52.60	—	—	78.91	78.85	222.1	—	13.930	7.179
—	—	—	—	79.27	79.21	221.0	—	13.924	7.182

Fluidities of Ternary Mixtures at 40°

% HNO ₃	% H ₂ SO ₄	Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{40/4}$	η cp.	ϕ abs.
		% HNO ₃	% H ₂ SO ₄						
50.26	12.31	—	—	273.28	272.09	437.0	1.3765	1.7514	57.10
—	—	—	—	273.24	272.06	437.0	—	1.7512	57.10
48.87	25.06	—	—	273.11	272.51	630.8	1.4747	2.5320	39.49
—	—	—	—	273.48	272.88	629.8	—	2.5314	39.50
50.93	36.90	—	—	44.35	44.07	94.3	—	3.3055	30.25
—	—	—	—	44.35	44.07	94.2	—	3.3019	30.29
47.16	52.60	—	—	59.61	59.49	156.9	—	7.425	13.47
—	—	—	—	59.27	59.16	158.2	—	7.444	13.43
—	—	—	—	59.61	59.50	156.7	—	7.416	13.48
—	—	—	—	59.27	59.16	158.2	—	7.444	13.43

TABLE XX
Fluidities of Ternary Mixtures at 10°

% HNO ₃	% H ₂ SO ₄	Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{10/4}$	η cp.	ϕ abs.
		% HNO ₃	% H ₂ SO ₄						
59.35	12.00	59.33	12.05	274.75	274.46	913.1	1.4760	3.6915	27.07
59.30	12.10	—	—	274.37	274.08	914.5	—	3.6920	27.09
60.41	25.00	60.41	25.02	274.81	274.66	1287.0	1.5805	5.2067	19.21
60.40	25.05	—	—	274.39	274.24	1289.2	—	5.2076	19.20
61.30	38.24	61.29	38.22	59.70	59.66	280.5	1.7394	13.312	7.512
61.27	38.20	—	—	59.36	59.33	282.4	—	13.326	7.504

Fluidities of Ternary Mixtures at 20°

Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{10/4}$	η cp.	ϕ abs.
% HNO ₃	% H ₂ SO ₄						
59.33	12.05	274.38	273.89	697.6	1.4616	2.8143	35.53
—	—	274.76	274.27	696.6	—	2.8142	35.53
60.41	25.02	274.42	274.17	1002.6	1.5662	4.0489	24.70
—	—	274.82	274.57	1001.1	—	4.0488	24.70
61.29	38.22	59.97	59.90	193.5	1.7249	9.2188	10.85
—	—	59.63	59.56	195.3	—	9.2518	10.81

Fluidities of Ternary Mixtures at 40°

Mean		Po gr/cm ²	P gr/cm ²	Time seconds	$\rho^{40/4}$	η cp.	ϕ abs.
% HNO ₃	% H ₂ SO ₄						
59.33	12.05	274.37	273.20	450.7	1.4323	1.8137	55.14
—	—	274.75	273.58	450.1	—	1.8138	55.13
61.41	25.02	274.83	274.20	630.8	1.5371	2.5477	39.25
—	—	274.43	273.80	632.4	—	2.5505	39.21
61.29	38.22	60.06	59.91	106.6	1.6901	5.080	19.69
—	—	59.72	59.57	107.3	—	5.084	19.67
—	—	60.06	59.91	106.5	—	5.075	19.70
—	—	59.72	59.69	107.4	—	5.099	19.61

Using the data in Tables X, XI, and XII for mixtures containing approximately 12.5 percent nitric acid, curves were drawn plotting fluidity against percentage H₂SO₄. From these curves the fluidity values at intervals of exactly 12.5 percent

sulfuric acid were read off. The data in Table XIII, XIV, and XV for mixtures containing approximately 25.0% nitric acid were similarly treated, i. e., the fluidity values were plotted against the percentage of sulfuric acid and the fluidity values read off at intervals of 12.5% H_2SO_4 . The data in Tables XVI, XVII, and XVIII for mixtures containing 37.5% nitric

TABLE XXI
Fluidities of Ternary Mixtures at 10°

% HNO_3	% H_2SO_4	Mean		P gr/cm ²	P gr/cm ²	Time sec.	ρ t/4	η cp.	ϕ abs.
		% HNO_3	% H_2SO_4						
73.25	—	73.27	12.90	37.56	37.33	105.5	1.5973	3.1327	31.92
73.28	12.90	—	—	37.24	37.01	106.3	—	3.1297	31.95
72.80	26.50	72.86	26.49	38.23	38.05	121.1	1.6334	3.6653	27.28
72.92	26.48	—	—	37.91	37.73	122.3	—	3.6709	27.24
85.72	13.60	85.41	13.60	38.06	37.70	84.9	1.6098	2.5462	39.27
85.39	13.60	—	—	37.74	37.39	85.5	—	2.5428	39.32

Fluidities of Ternary Mixtures at 20°

73	—	73.27	12.90	37.64	37.26	82.9	—	2.457	40.70
—	—	—	—	37.32	36.96	83.2	—	2.446	40.88
—	—	72.86	26.49	38.21	37.92	94.3	1.6161	2.8443	35.16
—	—	—	—	37.79	37.51	95.4	—	2.8462	35.13
—	—	85.41	13.60	38.05	37.50	68.1	1.5934	2.0314	49.23
—	—	—	—	37.73	37.19	68.7	—	2.0324	49.20

Fluidities of Ternary Mixtures at 40°

—	—	73.27	12.90	37.72	36.91	55.8	—	1.6384	61.04
—	—	—	—	37.40	36.61	56.3	—	1.6395	60.99
—	—	72.86	26.48	38.21	37.53	61.3	1.5839	1.8300	54.65
—	—	—	—	37.79	37.12	61.9	—	1.8279	54.70
—	—	85.41	13.60	38.11	36.98	47.0	—	1.3825	72.33
—	—	—	—	37.79	36.68	47.5	—	1.3860	72.15

acid and in Tables XIX, XX, and XXI for mixtures containing approximately 50.0, 62.5, 75.0, and 87.5% nitric acid were treated in the same manner. In this way the fluidity values were corrected for the deviations of the percentages of sulfuric acid from the desired concentrations.

The same method was employed to correct the fluidity values for the deviations of the nitric acid concentrations from the desired compositions. All mixtures in Table XXII having 12.5% HNO_3 were taken, and the fluidity plotted against

TABLE XXII
Values Read from Curves

% HNO_3	% $\text{H}_2\text{S}_4\text{O}$	Fluidity Absolute		
		10°	20°	40°
10.46	12.50	58.05	74.05	108.15
12.56	25.00	36.50	46.85	67.20
12.97	37.50	23.25	30.35	44.60
12.61	50.00	12.75	17.00	26.95
12.51	62.50	5.75	8.10	14.15
11.93	75.00	3.00	4.60	9.25
12.24	87.50	1.55	2.50	5.40
23.38	12.50	45.25	59.15	86.40
25.64	25.00	28.20	36.00	54.85
24.40	37.50	15.90	21.25	33.00
24.76	50.00	8.55	1.85	20.05
24.04	62.50	4.65	6.80	12.70
27.18	75.00	1.65	2.65	5.95
38.77	12.50	34.50	44.00	65.85
33.42	25.00	23.70	30.70	46.60
35.21	37.50	13.05	17.65	28.20
35.25	50.00	7.20	10.40	17.25
37.17	62.50	2.50	3.65	8.35
50.26	12.50	28.45	36.95	56.75
48.87	25.00	18.75	24.90	39.65
50.93	37.50	11.60	16.00	26.75
47.16	50.00	5.90	8.70	15.45
59.33	12.50	26.80	35.10	54.65
60.41	25.00	19.20	24.65	39.25
61.29	37.50	8.30	12.10	21.15
73.27	12.50	32.20	41.10	61.45
72.86	25.00	27.55	35.50	55.10
85.40	12.50	40.05	50.05	73.50

the percentage of nitric acid. The fluidity values at intervals of 12.5% HNO_3 were then read from the curves. All mixtures in Table XXII containing 25%, or 37.5% or 50.0%, etc., of sulfuric acid were similarly treated. The values obtained are

TABLE XXIII

Fluidity Values after Correction for the Deviations from the Desired Composition

% HNO ₃	% H ₂ SO ₄	Fluidity Absolute		
		10°	20°	40°
0.00	12.50	54.35	69.40	102.3
12.50	12.50	57.50	72.95	106.6
25.00	12.50	42.90	56.85	83.55
37.50	12.50	34.85	45.00	67.25
50.00	12.50	28.65	37.00	57.00
62.50	12.50	27.15	35.60	55.00
75.00	12.50	33.25	42.25	63.10
87.50	12.50	41.40	52.35	75.80
0.00	25.00	43.95	57.15	87.80
12.50	25.00	36.50	46.90	67.35
25.00	25.00	28.60	36.60	55.50
37.50	25.00	22.00	28.50	43.55
50.00	25.00	18.55	24.60	39.40
62.50	25.00	20.10	25.75	40.30
75.00	25.00	29.25	37.90	59.20
0.00	37.50	31.85	40.05	61.50
12.50	37.50	23.55	30.85	45.10
25.00	37.50	15.70	20.95	32.65
37.50	37.50	12.70	17.10	27.65
50.00	37.50	11.85	16.10	26.90
62.50	37.50	7.75	11.55	20.10
0.00	50.00	20.45	27.20	39.90
12.50	50.00	12.85	17.10	27.00
25.00	50.00	8.40	11.85	20.00
37.50	50.00	6.90	10.15	16.80
50.00	50.00	5.40	8.25	15.05
0.00	62.50	11.60	15.30	23.90
12.50	62.50	5.75	8.10	14.50
25.00	62.50	2.40	4.20	9.45
37.50	62.50	2.60	3.70	8.35
0.00	75.00	4.85	6.95	12.00
12.50	75.00	2.95	4.50	9.05
25.00	75.00	1.80	2.85	6.30
0.00	87.50	2.50	3.90	7.60
12.50	87.50	1.55	2.55	5.45
0.00	100.00	3.00	4.50	7.90
100.00	0.00	96.40	113.9	147.1

given in Table XXIII where the original values have been corrected for the deviations of both the nitric and sulfuric acids from the desired concentrations.

The results are shown graphically in Figure 5 which represents the effect of replacing water by nitric acid in mixtures containing a constant percentage of sulfuric acid.

Curves 1, 1' and 1'' in Figure 5 for 40°, 20°, and 10°, respectively, represent the effect of replacing water by nitric acid in a mixture containing 12.5 percent sulfuric acid, i. e., Curve 1 for 40° starts at (12.5% H_2SO_4 , 87.5% H_2O), passes through the points (12.5% H_2SO_4 , 12.5% HNO_3 , 75.0% H_2O), (12.5% H_2SO_4 , 25.0% HNO_3 , 62.5% H_2O)..... and ends at the point (12.5% H_2SO_4 , 87.5% HNO_3).

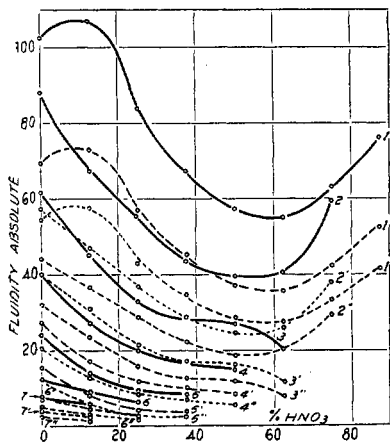


Fig. 5

Fluidity-Weight Concentration of Nitric Acid Curves for Ternary Mixtures Containing Constant Percentages of Sulfuric Acid

The first effect of replacing water by nitric acid is to increase the fluidity, producing a so-called "negative viscosity" effect which is equally well pronounced at all temperatures. This can only be ascribed partly to the action of the nitric acid

on the associated water molecules as seen in Figure 2 and must be largely due to some other dissociating influence of the nitric acid. On further replacement of the water present by nitric acid the fluidity drops to a minimum and then increases. The decrease in fluidity is probably due to the nitric acid combining with a large portion of the water present in the mixture and thereby having its fluidity reduced. On further substitution of nitric acid by water the amount of unhydrated molecules of nitric acid increases and the fluidity is raised.

Curves 2, 2' and 2'' for 40°, 20° and 10°, respectively, show the result of replacing water by nitric acid in a mixture containing 25 percent sulfuric acid, i. e., Curve 2 for 40° starts at the point (25.0% H_2SO_4 , 75.0% H_2O), passes through the points (25.0% H_2SO_4 , 12.5% HNO_3 , 62.5% H_2O), (25.0% H_2SO_4 , 25.0% HNO_3 , 50.0% H_2O). and ends at the point (25.0% H_2SO_4 , 75.0% HNO_3). The first replacement

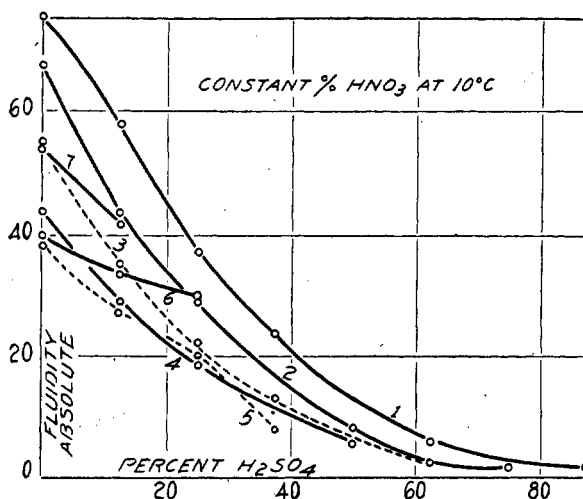


Fig. 6

Fluidity-Weight Concentration of Sulfuric Acid Curves
for Ternary Mixtures Containing Constant Percentages of
Nitric Acid

of water by nitric acid now produces no negative curvature. With Curves 2, 2' and 2'' as with Curves 1, 1' and 1'' the fluidity drops to a minimum and then increases. The decrease in fluidity is probably due as before to the nitric acid combining with the water present, and the increase in fluidity produced by replacement of most of the water present by nitric acid means an increase in the number of molecules of unhydrated nitric acid.

In Curves 3, 3' and 3'' which show the effect of substituting nitric for water in a mixture containing 37.5 percent

sulfuric acid (the curve starting at the point 37.5% H_2SO_4 , 62.5% H_2O and ending at the point 37.5% H_2SO_4 , 62.5% HNO_3) the first replacement of water by nitric acid lowers the fluidity. With further replacement of water the number of unhydrated nitric acid molecules increases which tends to raise the fluidity, and in the mixture having a high concentra-

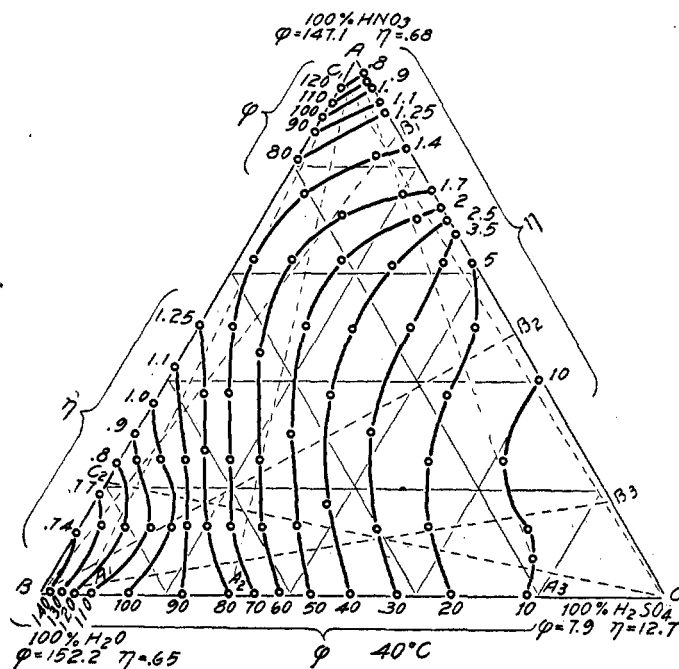


Fig. 7

Isorrhes for 40°

tion of acid a combination of the two acids probably takes place which tends to lower the fluidity. Where these opposite effects balance we have a region of nearly constant fluidity as in Curves 3, 3' and 3". In the curves previously discussed any combination of the two acids, taking place in the strongly acid mixtures, was not sufficient counteracted by the increase in fluidity due to the increasing concentration of free nitric

acid molecules, but in Curves 3, 3' and 3'' the increase in the concentration of free nitric acid molecules no longer offsets the effect produced by the combination of the two acids and the curves no longer show a minimum.

In Curves (4, 4', 4''), (5, 5', 5''), (6, 6', 6''), and (7, 7', 7''), the replacement of water by nitric acid causes a gradual decrease in fluidity. Here again the combination of the two acids in the highly acid mixtures more than offsets the increase in

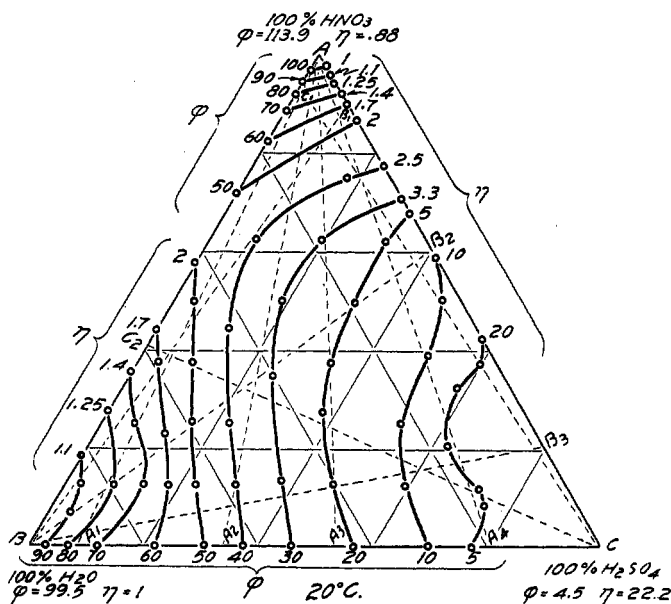


Fig. 8

Isorrhes for 20°

the concentration of unhydrated nitric acid molecules.

Figure 6 shows the effect of replacing water by sulfuric acid in a mixture containing a constant percentage of nitric acid. As no significant temperature variations were noted only the curves for 10° are given.

Curve 1 represents the effect of replacing water by sulfuric acid in a mixture containing 12.5 percent nitric acid, i. e.,

the curve starts at the point (12.5% HNO_3 , 87.5% H_2O) and ends at the point (12.5% HNO_3 , 87.5% H_2O). Because of the wide difference in fluidities of the water and of the sulfuric acid, which is substituted for it, the replacement of water rapidly increases the viscosity. With increasing concentration of sulfuric acid the combination between the two acids accounts for part of the increase in viscosity.

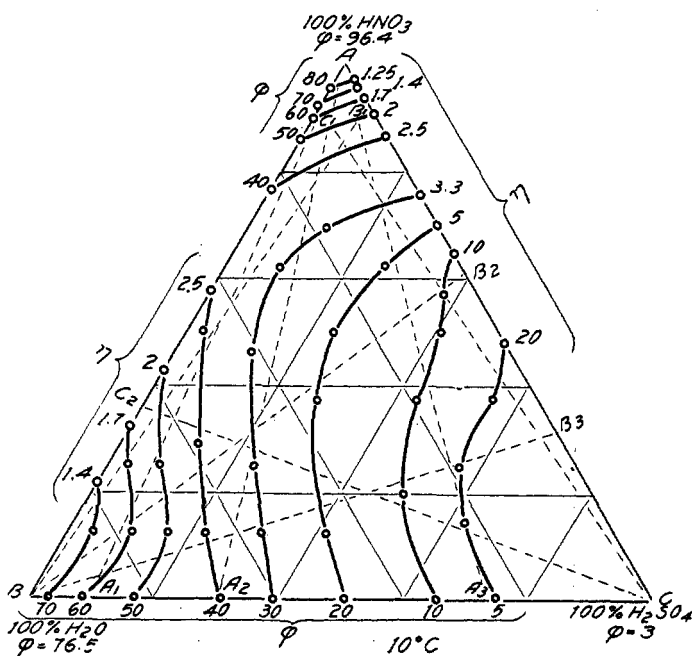


Fig. 9

Isorrhes for 10°

Curves 2, 3, 4, 5, 6 and 7 show the effect of replacing water by sulfuric acid in mixtures containing 25%, 37.5%, 50%, 62.5%, 75% and 87.5%, respectively. In all these curves the replacement of the highly fluid water by the highly viscous sulfuric acid causes a decrease in fluidity. Combination of the two acids, and a dehydration of the nitric acid as

suggested by Saposchnikow¹ probably are responsible for a part of the decrease in the more strongly acid mixtures.

Isorrheic Mixtures

At the suggestion of Professor John R. Crawford the curves representing mixtures of equal fluidity will be referred

TABLE XXIV
Composition of Ternary Mixtures Having the Same Fluidities

Fluidity	10°		20°		40°	
	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄
5	12.50	65.25	12.50	72.50	—	—
—	25.00	56.30	25.00	60.40	—	—
—	37.50	55.50	37.50	59.90	—	—
—	14.70	62.50	20.75	62.50	—	—
—	0.00	74.65	0.00	77.25	—	—
—	48.00	52.00	42.15	57.85	—	—
—	—	—	9.15	75.00	—	—
10	12.50	54.20	12.50	59.15	12.50	72.30
—	25.00	47.00	25.00	52.50	25.00	61.55
—	37.50	43.00	37.50	50.10	37.50	60.05
—	50.00	41.10	50.00	47.00	—	—
—	62.50	35.50	—	—	—	—
—	3.00	62.50	8.60	62.50	22.35	62.50
—	19.70	50.00	39.20	50.00	—	—
—	57.10	37.50	—	—	—	—
—	0.00	65.00	—	—	0.00	78.40
—	64.65	35.35	—	—	40.75	59.25
20	12.50	41.30	12.50	47.10	12.50	55.60
—	25.00	33.00	25.00	38.60	25.00	50.00
—	37.50	27.35	37.50	33.90	37.50	46.20
—	50.00	23.50	50.00	31.75	50.00	44.65
—	62.50	25.30	62.50	30.70	—	—
—	0.70	50.00	8.30	50.00	4.50	62.50
—	17.70	37.50	27.35	37.50	—	—
—	43.40	25.00	—	—	—	—
—	62.00	25.00	—	—	—	—
—	0.00	50.60	0.00	56.90	0.00	66.05
—	70.00	30.00	67.60	32.40	62.10	37.90

¹ Saposchnikow: loc. cit.

Fluidity	10°		20°		40°	
	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄
30	12.50	30.90	12.50	38.25	12.50	47.75
—	25.00	23.60	25.00	29.95	25.00	40.00
—	37.50	16.70	37.50	23.60	37.50	35.40
—	50.00	11.30	50.00	19.00	50.00	34.30
—	62.50	8.75	62.50	19.50	62.50	32.80
—	75.00	22.45	—	—	—	—
—	3.25	75.00	13.35	37.35	30.50	37.50
—	22.80	25.00	34.80	25.00	9.10	50.00
—	—	—	68.20	25.00	—	—
—	46.45	12.50	—	—	—	—
—	69.40	12.50	—	—	—	—
—	0.00	39.00	0.00	45.90	0.00	57.40
—	75.60	24.40	70.70	29.30	67.70	32.30
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40	12.50	22.30	12.50	29.95	12.50	40.80
—	25.00	14.90	25.00	22.30	25.00	32.85
—	37.50	8.80	37.50	15.70	37.50	27.45
—	50.00	2.65	50.00	10.25	50.00	24.40
—	—	—	62.50	8.00	62.50	25.25
—	—	—	75.00	17.70	—	—
—	—	—	0.15	37.50	—	—
—	6.75	25.00	20.75	25.00	47.10	25.00
—	—	—	—	—	61.80	25.00
—	28.75	12.50	44.25	12.50	—	—
—	—	—	71.65	12.50	—	—
—	0.00	30.60	—	—	0.00	49.95
—	57.70	0.00	—	—	—	—
—	76.65	0.00	—	—	—	—
—	86.50	13.50	—	—	70.15	29.85
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50	12.50	16.35	12.50	23.10	12.50	34.65
—	25.00	8.20	25.00	16.30	25.00	27.80
—	37.50	2.75	37.50	9.60	37.50	21.30
—	—	—	50.00	3.80	50.00	17.10
—	—	—	—	—	62.50	16.60
—	—	—	—	—	8.60	37.50
—	—	—	8.70	25.00	29.75	25.00
—	—	—	—	—	70.20	25.00
—	19.60	12.50	31.60	12.50	—	—
—	—	—	84.75	12.50	—	—
—	42.80	0.00	57.70	0.00	—	—
—	85.75	0.00	71.65	0.00	—	—
—	0.00	16.70	0.00	30.90	0.00	43.60
—	90.85	9.15	86.10	13.90	72.30	27.70

Fluidity	10°		20°		40°	
	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄
60	12.50	10.75	12.50	18.20	12.50	29.00
—	25.00	3.20	25.00	10.75	25.00	23.00
—	—	—	37.50	3.85	37.50	15.95
—	—	—	—	—	50.00	10.75
—	—	—	—	—	62.50	8.80
—	—	—	—	—	75.00	20.95
—	—	—	—	—	1.10	37.50
—	—	—	—	—	20.25	25.00
—	—	—	22.75	12.50	45.10	12.50
—	—	—	—	—	71.05	12.50
—	32.10	0.00	43.90	0.00	—	—
—	89.90	0.00	82.25	0.00	—	—
—	0.00	8.65	0.00	22.05	0.00	38.20
—	93.60	6.40	89.80	10.20	75.60	24.40
70	12.50	4.30	12.50	13.90	12.50	23.95
—	—	—	25.00	5.95	25.00	18.60
—	—	—	—	—	37.50	11.40
—	—	—	—	—	50.00	5.10
—	—	—	—	—	62.50	2.10
—	—	—	—	—	75.00	4.30
—	—	—	—	—	10.25	25.00
—	—	—	0.65	12.50	34.95	12.50
—	—	—	—	—	82.00	12.50
—	21.60	0.00	35.35	0.00	—	—
—	93.00	0.00	88.80	0.00	—	—
—	0.00	3.00	0.00	12.50	0.00	34.50
—	95.25	4.75	92.00	8.00	83.45	16.55
80	—	—	12.50	8.95	12.50	20.40
—	—	—	25.00	1.30	25.00	14.10
—	—	—	—	—	37.50	7.30
—	—	—	—	—	50.00	0.15
—	—	—	—	—	4.20	25.00
—	—	—	—	—	27.20	12.50
—	—	—	27.80	0.00	50.20	0.00
—	95.50	0.00	91.75	0.00	81.10	0.00
—	—	—	0.00	6.75	0.00	30.20
—	97.00	3.00	93.80	6.20	90.10	9.90

Fluidity	10°		20°		40°	
	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄
90	—	—	12.50	3.10	12.50	17.15
—	—	—	—	—	25.00	9.90
—	—	—	—	—	37.50	3.20
—	—	—	—	—	22.50	12.50
—	—	—	18.30	0.00	42.40	0.00
—	98.25	0.00	94.35	0.00	86.50	0.00
—	—	—	0.00	3.05	0.00	22.80
—	98.80	1.20	95.40	4.60	92.05	7.95
100	—	—	—	—	12.50	14.40
—	—	—	—	—	25.00	6.25
—	—	—	—	—	18.35	12.50
—	—	—	87.50	9.30	—	—
—	—	—	—	—	35.75	0.00
—	—	—	96.85	0.00	89.20	0.00
—	—	—	—	—	0.00	14.15
—	—	—	97.20	2.80	94.45	5.55
110	—	—	—	—	12.50	11.15
—	—	—	—	—	25.00	2.65
—	—	—	—	—	29.80	0.00
—	—	—	99.30	0.00	91.80	0.00
—	—	—	—	—	0.00	8.45
—	—	—	99.15	0.85	96.10	3.90
120	—	—	—	—	12.50	7.20
—	—	—	—	—	24.10	0.00
—	—	—	—	—	94.25	0.00
—	—	—	—	—	0.00	5.30
—	—	—	—	—	97.50	2.50
130	—	—	—	—	12.50	3.45
—	—	—	—	—	18.05	0.00
—	—	—	—	—	96.60	0.00
—	—	—	—	—	0.00	3.00
—	—	—	—	—	98.55	1.45

Fluidity	10°		20°		40°	
			% HNO ₃	% H ₂ SO ₄	% HNO ₃	% H ₂ SO ₄
140	—	—	—	—	11.10	0.00
—	—	—	—	—	98.60	0.00
—	—	—	—	—	0.00	1.50
—	—	—	—	—	99.35	0.65
150	—	—	—	—	2.15	0.00
—	—	—	—	—	0.00	0.30

to as isorrhes (or isorrheals). The data for the isorrheic mixtures were interpolated from Figures 2, 3, 4, 5, 6, and from the curves similar to those of Figure 6 for 20° and 40°. The data so obtained are given in Table XXIV and shown graphically in Figures 7, 8 and 9.

From these curves the same relationships plotted in Figures 5 and 6 can be read off. For example, if in Figure 7 we pass from left to right along the straight line which contains 10% HNO₃, we find that replacing water by sulfuric acid in a mixture which contains 10% HNO₃ lowers the fluidity in a regular manner until the mixture contains about 30% H₂SO₄ when further replacements of water by sulfuric acid decrease the fluidity much less rapidly. If we read from bottom to top on the line containing 10% H₂SO₄ we see that replacing water by nitric acid in a mixture containing 10% H₂SO₄ decreases the fluidity until a minimum is reached at around 40 to 50 fluidity units, after which further replacements of water by nitric acid increase the fluidity.

As any line drawn from one of the apices to the opposite side, such as AA₁, AA₂, BB₁, etc., indicates a constant ratio of the other two components, the effect of adding one component to any mixture of the other two can be readily seen.

By referring to the line AA₁, Figure 7, it is seen that the first effect of adding absolute nitric acid to a mixture containing 93% H₂O and 7% H₂SO₄ is to increase the fluidity, giving negative curvature. On further addition of nitric acid the

fluidity decreases to a minimum, after which any addition of nitric acid raises the fluidity. When nitric acid is added to a mixture of water and sulfuric acid containing between 20 to 70% H_2SO_4 , the fluidity steadily decreases to a minimum after which it is increased by further additions of nitric acid (line AA_2). As the amount of sulfuric acid in the original mixture is increased, the amount of nitric acid, which must be added in order to reach the point, of minimum fluidity, steadily decreases. When nitric acid is added to a mixture of sulfuric acid and water containing over 80% H_2SO_4 , the fluidity is increased only slightly as is seen in line AA_3 , Figure 7. It is interesting to note that negative curvature is found on adding absolute nitric acid to mixtures of sulfuric acid and water, which contain either a large excess of water (line AA_1) or a large excess of acid (line AA_3). This negative curvature cannot very well be ascribed to a decomposition of either the associated water molecules or the associated sulfuric acid molecules, for, as is seen in Figure 2, only an exceedingly slight negative curvature is exhibited on adding nitric acid to water, and no trace of negative curvature is found on adding nitric acid to sulfuric acid (Figure 4). Any attempt to explain the negative curvature as due to a dissociation of the sulfuric acid-water complexes by the nitric acid, meets with the objection that no negative curvature is found when nitric acid is added to mixtures of sulfuric acid and water containing between 20% and 80% H_2SO_4 . As the concentration of the sulfuric acid-water complexes is greatest in such mixtures, the dissociation of the complexes and the negative curvature should be also most pronounced.

On adding sulfuric acid to mixtures of nitric acid and water as in lines CC_1 and CC_2 the fluidity steadily decreases. On adding sulfuric acid to mixtures of nitric which are rich in nitric acid (line CC_1) the fluidity drops much more rapidly, as seen by the closer spacing of the isorrhes, than when sulfuric acid is added to mixtures rich in water (line CC_2). As nitric acid and water have approximately the same fluidity,

this effect must be due either to a combination of the nitric acid and sulfuric acid or some other chemical change such as suggested by Saposchnikow.

On adding water to a mixture of nitric acid and sulfuric acid containing over 70% HNO_3 (line BB_1), the fluidity falls to a minimum and then increases, a behavior which resembles that of nitric acid on the addition of water. When water is added to mixtures of sulfuric acid and nitric acid containing over 30% HNO_3 (line BB_2), the result produced is similar to that of adding water to sulfuric acid, in that the fluidity steadily increases.

Conclusions

1. The fluidities of forty-five binary and ternary mixtures of nitric acid, sulfuric acid, and water have been measured at the temperatures of 10°, 20°, and 40° C.

2. Several cases of both negative and positive curvature of the fluidity-volume concentration curves have been observed. The evidence favors the view that negative curvature is due to some form of dissociation while positive curvature is brought about by solvation.

3. The concentration of the mixture showing the maximum deviation from the linear fluidity-volume concentration curve is independent of the temperature, provided that only one solvate is formed, and in such favorable cases it is believed that this concentration may be utilized for finding the composition of the solvate.

4. Concentrations of equal fluidity (isorrhies), differing by intervals of ten absolute units, have been calculated for each of the three temperatures and plotted on triangular diagrams given herewith.

Easton, Pa.
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