

pure liquids. In the present communication the study of the second point—the factors affecting the ionic disintegration of solvent-solute complexes in solution—has been started, and additional generalizations⁴¹ deduced. These generalizations have been shown to be in excellent qualitative agreement with the experimental data of earlier investigators. A more stringent test of their validity has been successfully sought by careful conductivity determinations on specially selected systems, as described in the article immediately succeeding.

The connection between the ionization hypothesis here presented and the views of Abegg and Bodländer on the one hand, and of Werner on the other, has been briefly examined and some points of difference indicated.

In a future article the factors affecting the formation and stability of addition compounds in solution will be further discussed, and the problem of strong electrolytes investigated.

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COMPOUND FORMATION AND SPECIFIC CONDUCTIVITY IN SOLUTIONS OF THE TYPES ACID:ESTER, ACID:KETONE AND ACID:ACID.

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As explained in the preceding article,¹ the purpose of this investigation is to test, more stringently than can be done by existent data, the general validity of the hypothesis that ionization in solutions is dependent upon preliminary compound formation between solvent and solute. Careful conductivity determinations through the whole concentration range (pure solvent to pure solute) have here been carried out upon several series of typical two-component systems, for the different members of which the relative extent of compound formation in the liquid state has already been established by a study of their freezing-point curves.

For the first series, systems of the general type $HX:R.COOR'$ were chosen. It has been shown previously² that, in such systems, the extent of compound formation increases regularly as the radicals R and R' of the ester are made more electropositive, or as the radical X of the acid is made more electronegative. A suitable variation of all 3 radicals has been ensured in this work by selecting the following systems for examination:

⁴¹ See pp. 1420–22.

¹ Kendall and Gross, *THIS JOURNAL*, **43**, 1416 (1921).

² Kendall and Booge, *ibid.*, **38**, 1712 (1916).

acetic acid (a typical weak acid) and trichloro-acetic acid (a typical strong acid) with each of the 3 esters, ethyl acetate, ethyl benzoate and benzyl benzoate.

For the second series, systems of the general type, $HX:R.CO.R'$ were taken. Freezing-point data for such systems show³ that here also the extent of compound formation increases as the radicals R and R' of the ketone are made more electropositive, or as the radical X of the acid is made more electronegative. The following representative systems were studied: acetic acid and trichloro-acetic acid with acetone and acetophenone.

For the third series, systems of the general type, $HX:HY$ were selected. Compound formation between acids in pairs has been shown⁴ to increase regularly with increasing diversity in the electro-affinity of the radicals X and Y. In this work acetic acid was taken as the fixed component HX, and acids of widely divergent character (trichloro-acetic, a typical strong acid; monochloro-acetic, a typical transition acid; and propionic, a typical weak acid similar to acetic) chosen as the variable component HY. A considerable range in compound formation through the series was thus obtained. This series was also still further extended by including some examples of the type, acid: base, for which reliable data are already available.⁵ An additional system of this class, acetic acid:formamide, was here investigated for comparison.

Experimental.

Purification of Materials.—The nature of the experimental work rendered is necessary to take extreme precautions to ensure the elimination of even minute traces of impurities from all substances employed. The presence of impurities in quantities insufficient to exert any appreciable influence upon the freezing point or boiling point was frequently found to result in a very considerable change in specific conductivity.⁶ A constant specific conductivity was therefore made the final criterion of purity. After other satisfactory physical constants had been obtained, purification was continued until no further lowering in the specific conductivity could be effected. Brief descriptions of the methods of purification adopted will be found under the separate systems below. Here the measure of success attained may be indicated by comparing the results of this work with the lowest values previously recorded. The association factors⁷ and viscosities⁸ for each liquid are included for convenience of reference in subsequent discussion.

³ Kendall and Gibbons, *THIS JOURNAL*, **37**, 149 (1915).

⁴ Kendall, *ibid.*, **36**, 1722 (1914).

⁵ Patten, *J. Phys. Chem.*, **6**, 580 (1902).

⁶ See also Walden, *Z. physik. Chem.*, **46**, 121 (1903); Schlesinger and Martin, *THIS JOURNAL*, **36**, 1592 (1914); Davis, Putnam and Jones, *J. Franklin Inst.*, **180**, 577 (1915).

⁷ Walden, *Z. physik. Chem.*, **39**, 561 (1902).

⁸ Kendall and Wright, *THIS JOURNAL*, **42**, 1776 (1920); unpublished data by Kendall and Brakeley; Merry and Turner, *J. Chem. Soc.*, **105**, 758 (1914).

TABLE I.—SPECIFIC CONDUCTIVITIES OF PURE LIQUIDS.

Liquid.	Association factor.	η_{25° .	κ_{25° (Kendall and Gross).	κ_{25° (previous record).
Ethyl acetate ⁹	1.00	0.004239	$<1 \times 10^{-9}$	4×10^{-7}
Ethyl benzoate.....	1.00	0.02014	$<1 \times 10^{-9}$
Benzyl benzoate.....	1.00	0.08514	$<1 \times 10^{-9}$
Acetone ¹⁰	1.26	0.003065	5.8×10^{-8}	15×10^{-8}
Acetophenone ¹¹	1.16	0.01681	5.5×10^{-8}	18×10^{-8}
Acetic acid ¹²	3.62	0.01121	2.4×10^{-8}	2×10^{-8}
Propionic acid ¹³	> 1.0	0.0102	$<1 \times 10^{-9}$	7×10^{-8}
Monochloro-acetic acid. > 1.0	1.4×10^{-6} (60°)
Trichloro-acetic acid ¹⁴ .	> 1.0	0.0397 (60°)	6.2×10^{-9} (60°)	1×10^{-7} (60°)
Formamide ¹⁵	6.18	0.03358	4×10^{-6}	3×10^{-6}

Temperature Regulation.—Wherever practicable, determinations were carried out at 25°, in a large Freas thermostat electrically regulated to $\pm 0.01^\circ$. In the case of solutions containing considerable excess of trichloro-acetic or monochloro-acetic acid, it was not possible to obtain direct measurements at 25°, since the systems start to solidify above that temperature, and supercooling to any large extent in the presence of the platinum electrodes could not be successfully maintained. The curves for systems containing these acids as one component were consequently completed by carrying out determinations, where necessary, at a higher temperature (60°) and transposing the results so obtained to values approximately correct for 25° by the use of a temperature coefficient derived from the last solution measurable at the lower temperature. The assumption that the temperature coefficient is independent of concentration renders, of course, such transposed values rather uncertain, but as will be seen by reference to the diagrams¹⁶ the portions of the curves so treated are of only minor importance, and the results obtained are sufficiently accurate to indicate the essential course of the completed curves. The determinations at 60° were carried out in a smaller thermostat, fitted with an Ostwald regulator and showing variations in temperature of less than $\pm 0.05^\circ$.

Conductivity Measurements.—The specific conductivities of the solutions examined varied from 6×10^{-5} to less than 1×10^{-9} mhos, the latter value constituting the lower limit of the measurable range with the apparatus employed. In order to obtain good sound minima with the more poorly conducting solutions, cells of the

⁹ Kahlenberg and Lincoln, *J. Phys. Chem.*, **3**, 12 (1899). Sammis (*ibid.*, **10**, 593 (1906)) states that ethyl acetate shows zero conductivity, but does not indicate his limits of measurement.

¹⁰ Walden, *Z. physik. Chem.*, **73**, 263 (1910).

¹¹ Lincoln, *Trans. Wisconsin Acad.*, **12**, II, 395 (1898–9).

¹² Patten, *J. Phys. Chem.*, **6**, 654 (1902). It must be noted that Patten worked with cells possessing much larger constants than those here employed, and also used a short bridge. His value for κ can consequently be only an approximation, since it is right at the lower limit of measurable conductivities.

¹³ Otten, *Diss.*, München, 1887.

¹⁴ Whetham, *Phil. Mag.*, [5] **44**, 1 (1897). The material employed was evidently very impure, since its m. p. (52°) was more than 7° below that of the acid used in this work.

¹⁵ Davis and Putnam, *J. Franklin Inst.*, **180**, 577 (1915). Only a very small fraction of material with $\kappa = 3 \times 10^{-6}$ was obtained by these investigators, the formamide actually employed in their conductivity measurements having much higher values, $\kappa = 7 \times 10^{-6}$ to 15×10^{-6} .

¹⁶ Dotted curves, in the diagrams, indicate values reduced from 60°.

special type described by Beans and Eastlack¹⁷ were used throughout. The electrodes were carefully platinized and the cell constants (which ranged, for different cells, between 0.007 and 0.009) were frequently redetermined during the course of the determinations. As noted by Beans and Eastlack, the passage of the current caused no appreciable heating effects with the solutions investigated. Capacity errors were tested for, and found to be within the errors of measurement.

The bridge employed was a 3-meter Leeds and Northrup instrument; the accuracy of the bridge calibrations and of the attached resistances was thoroughly checked throughout the work. Alternating current at 1000 cycles per second was obtained from a constant-speed high-frequency generator. The telephone receiver used was tuned to the same frequency.

Conductivity measurements were made, for each system, at a sufficient number of different concentrations to define the complete curve, the distance between successive points being varied to suit each particular case. Mixtures were made up by direct weighing, with the use of a Grethan pipet for the liquids. The molecular composition values tabulated below are accurate within $\pm 0.05\%$. The accuracy of the conductivity data does not approach this in order. For poorly conducting solutions ($\kappa < 10^{-7}$) the error limit is from 1 to 2×10^{-9} . For solutions of higher conductivity, the values given are accurate to 0.5 or 1.0% for systems of the types acid: ester and acid:acid, and from 1.0 to 2.0% for systems of the types acid: ketone and acid:base. The main source of error lies in the difficulty of preparing materials of constant purity. In particular cases (*i. e.*, in systems containing acetone or formamide) the limits of error may even exceed 2.0%, owing to the impossibility of keeping an adequately purified product entirely unchanged during the determinations. The problem here presents the same difficulties as does the preparation of ultra-conductivity water.¹⁸

Even the largest possible error which may thus be introduced, however, is negligible when the relative positions of the conductivity curves for different systems are compared, as will be seen below.

Systems of the Type, Acid: Ester.

Trichloro-acetic Acid: Ethyl Acetate.—Trichloro-acetic acid (reputed c. p.) was dissolved in hot benzene and precipitated as fine crystals by rapid cooling. The crystals were repeatedly washed with cold benzene and the washings drained off. The residual crystals, with adherent benzene, were then liquefied by heating and the hot solution poured into a crystallizing dish over 99% sulfuric acid in a vacuum desiccator. Crystals of trichloro-acetic acid were deposited on cooling, and the last traces of benzene were completely removed by absorption and sulfonation in the sulfuric acid. The melting point of the product thus obtained, 59.4° , is the highest yet recorded.¹⁹

¹⁷ Beans and Eastlack, *THIS JOURNAL*, **37**, 2674 (1915).

¹⁸ See Kendall, *ibid.*, **38**, 2460 (1916).

¹⁹ See Kendall and Booge, *ibid.*, **38**, 1723 (1916). Owing to the extremely tremely hygroscopic character of trichloro-acetic acid, work on systems in which it formed one component was restricted to dry, cold days. Considerable patience was occasionally necessary.

Ethyl acetate was purified by careful fractionation, according to the recommendations of Wade.²⁰ The sample employed gave a boiling point of $77.1 \pm 0.05^\circ$.

The specific-conductivity data for the complete system are given below. Compositions of mixtures are expressed in molecular percentages; conductivities are given in reciprocal ohms $\times 10^7$; the temperature is 25° unless otherwise noted. The results are also reproduced graphically in Fig. 1.

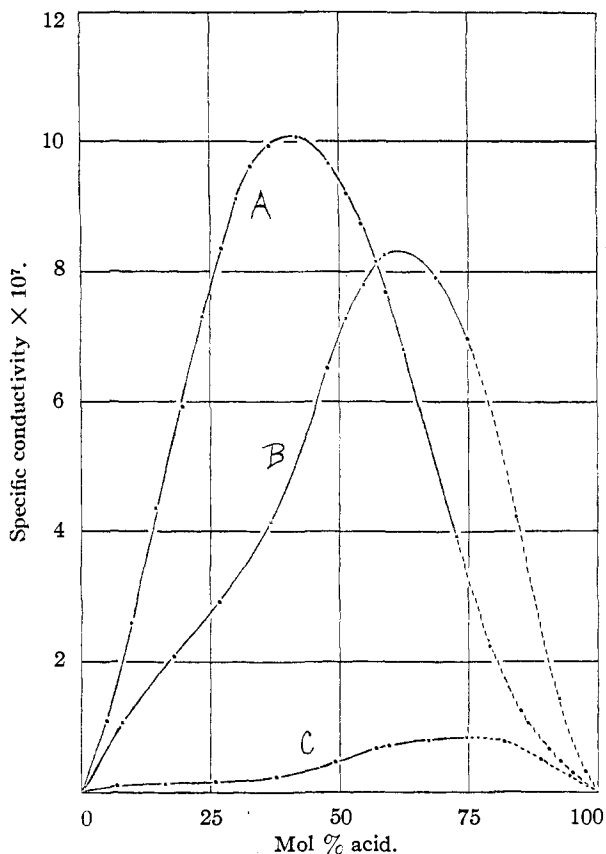


Fig. 1.—Systems of the type acid:ester. Curve A, trichloro-acetic acid:ethyl acetate; Curve B, trichloro-acetic acid:ethyl benzoate; Curve C, trichloroacetic acid:benzyl benzoate.

Mol % acid	0.0	4.93	9.80	14.36	19.55	23.56	27.31	30.07
$\kappa \times 10^7$	<0.01	1.10	2.59	4.36	5.94	7.32	8.37	9.12
Mol % acid	33.06	36.67	42.05	48.05	51.52	54.34	57.22	59.07
$\kappa \times 10^7$	9.62	9.95	10.05	9.67	9.19	8.74	8.11	7.68
Mol % acid	63.16	72.63	72.63	79.12	86.40	...		
$\kappa \times 10^7$	6.82	3.93	7.02(60°)	44.01 (60°)	1.91(60°)			
Mol % acid	94.66		100.0					
$\kappa \times 10^7$	0.37 (60°)		0.06(60°)					

²⁰ Wade, *J. Chem. Soc.*, 87, 1656 (1905).

Acetic Acid:Ethyl Acetate.—Acetic acid was first partially purified by successive fractional crystallizations of c. p. glacial acid. It is an exceedingly laborious and wasteful process to remove all traces of water by this method,²¹ consequently the following alternative procedure was devised. The freezing-point of a partially purified product was carefully determined and the water content calculated from the amount of divergence from the standard value, using the figures of De Visser.²² The exact quantity of redistilled acetic anhydride necessary for the conversion of this water to acetic acid was then added and complete hydrolysis effected by refluxing the liquid at the boiling point for 30 hours, taking care to exclude moisture.²³ The acid so obtained was carefully fractionated and the main fraction (b. p., 117.8° ± 0.1°; m. p., 16.57° ± 0.05°) employed in the conductivity work. The results are given below and in Fig. 1.

Mol % acid.....	0.00	23.52	49.27	77.87	100.0
$\kappa \times 10^7$	<0.01	0.05	0.12	0.20	0.24

Trichloro-acetic Acid: Ethyl Benzoate.—Ethyl benzoate, reputed c. p., was fractionated repeatedly under ordinary pressure. The fraction with constant boiling point 212.9° ± 0.1° was employed.²⁴

Mol % acid	0.00	7.95	17.93	26.83	36.59	47.66	51.37	54.81
$\kappa \times 10^7$	<0.01	1.19	2.08	2.91	4.14	6.32	7.28	7.80
Mol % acid	58.88	68.72	68.72	74.97	84.32	92.57	100.0	
$\kappa \times 10^7$	8.26	7.91	13.91	12.24	7.57	2.54	0.06	
			(60°)	(60°)	(60°)	(60°)	(60°)	

Acetic Acid: Ethyl Benzoate.—

Mol % acid.....	0.00	10.15	28.78	44.07	61.45	74.69	84.60	91.74	100.0
$\kappa \times 10^7$	<0.01	0.04	0.08	0.16	0.28	0.38	0.43	0.38	0.24

Trichloro-acetic Acid: Benzyl Benzoate.—Attempts to purify benzyl benzoate by distillation under ordinary pressure, as recommended by the Earl of Berkeley,²⁵ gave a product of inconstant specific conductivity, probably due to slight cracking at the high temperature required (corrected b. p., 323.0° ± 0.2°). An improved form of apparatus²⁶ for fractionation under constant low pressure (about 20 mm.) was devised, and a satisfactory product obtained by repeating the distillation of the best fraction until no further change in its physical constants could be effected.²⁷

²¹ See Bousfield and Lowry, *J. Chem. Soc.*, **99**, 1432 (1911); DeVisser, *Rec. trav. chim. Belg.*, **12**, 101 (1893). Ballo (*Z. physik. Chem.*, **72**, 439 (1910)) claims that acetic acid and water form solid solutions.

²² De Visser, *loc. cit.*, p. 118.

²³ Johnstone (*Trans. Nova Scotia Inst. Science*, **13**, 199 (1913-14)) attempted this method, but found the specific conductivity of his product higher than at first. This he attributed to traces of HCl in the anhydride employed; more probably, however, it was due to incomplete hydrolysis.

²⁴ Timmermans, *Bull. soc. chim. Belg.*, **25**, 316 (1911).

²⁵ Earl of Berkeley, *J. Chem. Soc.*, **109**, 520 (1916).

²⁶ See Gross and Wright, *J. Ind. Eng. Chem.*, **13**, 701 (1921).

²⁷ The m. p. of the final product was 19.3° ± 0.05°. Values as high as 21° are to be found in the literature (see Claisen, *Ber.*, **20**, 647 (1887)), but such values, being based without exception upon measurements made by the capillary-tube method upon small amounts of material with unstandardized thermometers, are worthless for comparison. More recent work establishes 19.4° ± 0.05° as the most probable m. p. for a perfectly pure product (see Kendall and Monroe, *THIS JOURNAL*, **43**, 115 (1921)).

Mol % acid	0.00	6.94	16.25	26.05	37.58	49.28	57.01	59.54	67.25
$\kappa \times 10^7$	<0.01	0.12	0.13	0.16	0.23	0.47	0.68	0.73	0.80
Mol % acid	74.72	74.72	81.96		88.96		94.50		100.00
$\kappa \times 10^7$	0.84	2.28 (60°)	2.17 (60°)		1.37 (60°)		0.70 (60°)		0.06 (60°)

Acetic acid : Benzyl Benzoate.—

Mol % acid.....		0.00	22.76	73.81	100.0
$\kappa \times 10^7$		<0.01	< 0.01	< 0.01	0.24

Systems of the Type, Acid : Ketone.

Trichloro-acetic Acid : Acetone.—The difficulties encountered in the purification of acetone have been noted by many previous investigators.²⁸ Impurities other than water can be removed by forming and separating the bisulfite addition compound, hydrolyzing, and fractionating repeatedly. The real task, however, still remains—the total elimination of water. The method proposed by Shipsey and Warner²⁹ was attempted, but the resulting product (although satisfactory in its other physical constants) possessed too high a specific conductivity for use in this work. The procedure finally resorted to was that recommended by Timmermans³⁰—dehydration by means of phosphorus pentoxide. Acetone of low conductivity was thus obtained and carefully fractionated. In spite of all precautions, however, it was found that the conductivity of the purest material prepared could not be kept constant, but increased slowly on standing.³¹ Freshly fractionated acetone was consequently always employed in the preparation of the solutions listed below, and conductivity measurements carried out as rapidly as possible, consistent with accurate work. Even so, great difficulty was experienced in duplicating some of the individual points in trichloro-acetic acid—acetone mixtures, the deviations between different preparations amounting in some cases to 5%. The uncertainty thus introduced in the conductivity data, however, does not affect their relative magnitude as compared with the values for other systems, as may be seen most readily by reference to Fig. 2.

Mol % acid	0.00	3.37	6.76	10.05	12.52	16.28	19.53	23.04	26.02
$\kappa \times 10^7$	0.58	88.6	128.4	163.0	198.5	214.5	222.9	224.8	218.9
Mol % acid	28.57	31.81	40.04	47.32	54.17	59.74	65.79	72.47	
$\kappa \times 10^7$	205.1	183.4	144.1	118.0	95.7	73.8	54.4	33.1	
Mol % acid	76.60		76.60		92.66		100.0		
$\kappa \times 10^7$	20.23		36.01 (60°)		2.57 (60°)		0.06 (60°)		

Acetic Acid : Acetone.—

Mol % acid.....	0.00	12.56	20.27	28.65	39.45	46.03	51.04	64.92
$\kappa \times 10^7$	0.58	3.02	3.46	4.19	4.42	4.58	5.08	4.80
Mol % acid.....	71.43	81.10	92.23	100.0				
$\kappa \times 10^7$	4.32	3.12	1.33	0.24				

²⁸ See, for example, Walden, *Z. physik. Chem.*, **46**, 124 (1903); Timmermans, *Bull. soc. chim. Belg.*, **24**, 244 (1910).

²⁹ Shipsey and Warner, *J. Chem. Soc.*, **103**, 1255 (1913).

³⁰ Timmermans, Reference 28. A considerable loss of material results from the action of the pentoxide on the acetone itself.

³¹ This increase may be accounted for either by the absorption of minute amounts of impurities which affect the conductivity tremendously (as CO₂ from the air does in the case of water) or by the steady progress of isomeric (keto-enol) or polymeric changes on standing.

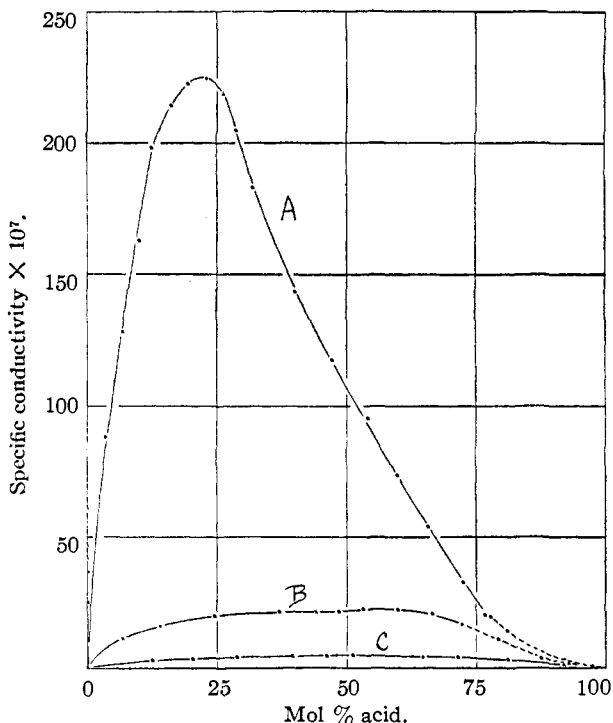


Fig. 2.—Systems of the type acid ketone. Curve A, trichloro-acetic acid:acetone; Curve B, trichloro-acetic acid:acetophenone; Curve C, acetic acid:acetone.

Trichloro-acetic Acid:Acetophenone.—Acetophenone (reputed c. p.) was dehydrated with phosphorus pentoxide and repeatedly fractionated³² under ordinary pressure. The material finally employed was of constant boiling point ($202.3^\circ \pm 0.1^\circ$), with specific conductivity³³ 5.5×10^{-8} .

The results given below are also reproduced graphically in Fig. 2.

Mol % acid	0.00	6.83	14.04	24.60	36.92	44.15	48.42	53.23
$\kappa \times 10^7$	0.55	11.39	15.96	20.10	21.35	21.41	21.66	22.38
Mol % acid	59.94	66.64	71.37	72.42	71.37	79.27	87.38	
$\kappa \times 10^7$	22.57	20.84	17.77	16.88	44.43 (60°)	27.94 (60°)	10.57 (60°)	
Mol % acid	95.16	100.0						
$\kappa \times 10^7$	1.48 (60°)	0.06 (60°)						

Acetic Acid:Acetophenone.—

Mol % acid	0.00	6.91	16.39	25.39	33.29	40.98	49.55	57.22
$\kappa \times 10^7$	0.55	2.86	3.33	3.51	3.58	3.46	3.44	3.20
Mol % acid	65.87	69.68	77.20	82.79	90.74	100.0		
$\kappa \times 10^7$	2.83	2.59	2.26	1.75	1.11	0.24		

³² The acetophenone was carefully decanted off from the pentoxide before distilling so as to avoid the possible formation of benzoic acid during fractionation. Compare Klago and Allendorf, *Ber.*, **31**, 1298 (1898).

³³ The value given here could probably be still further reduced, since very small fractions with somewhat lower conductivities were obtained.

Systems of the Type, Acid:Acid.

Trichloro-acetic Acid:Acetic Acid.—The results for this system are shown in graphic form in Fig. 3.

Mol % trichloro-acetic acid	0.00	4.86	10.43	18.72	23.72	27.67	31.75	37.99
$\kappa \times 10^7$	0.24	1.67	3.67	6.37	8.05	8.31	8.08	7.10
Mol % trichloro-acetic acid	44.87	52.39	60.39	68.34	71.73	71.73		
$\kappa \times 10^7$	5.64	3.80	2.25	1.15	0.84	2.91 (60°)		
Mol % trichloro-acetic acid	82.37			90.53		100.0		
$\kappa \times 10^7$	1.04 (60°)			0.38 (60°)		0.06 (60°)		

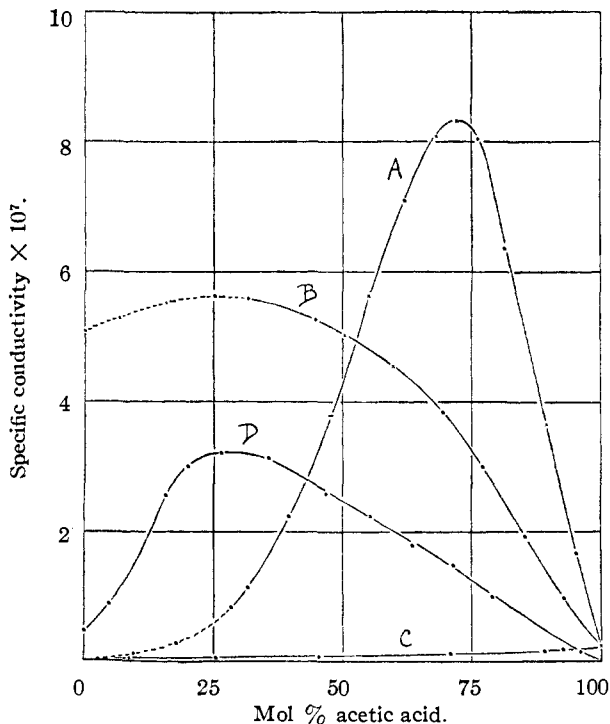


Fig. 3.—Systems of the type acid: acid. Curve A, trichloro-acetic acid:acetic acid; Curve B, monochloro-acetic acid:acetic acid; Curve C, propionic acid:acetic acid; Curve D, formamide:acetic acid(reduced to 1/200).

Monochloro-acetic Acid:Acetic Acid.—Monochloro-acetic acid was recrystallized from benzene and fractionated under atmospheric pressure. A large constant-boiling fraction was obtained, which was again crystallized several times from benzene, as described under trichloro-acetic acid.³⁴ The final product possessed an exceptionally high specific conductivity³⁵ for a pure substance, $\kappa_{80^\circ} = 1.4 \times 10^{-6}$. Further

³⁴ See p. 1429.

³⁵ No previous values are recorded in the literature. It is of interest to note, however, that the dielectric constant is also exceptionally high (Walden, *Z. physik. Chem.* 70, 569 (1909)).

attempts at purification, however, did not result in any reduction. The specific conductivity curve for the system is shown in Fig. 3.

Mol % monochloro-acetic acid	0.00	7.25	14.76	23.02	30.50	40.16	49.60	55.20
$\kappa \times 10^7$	0.24	0.98	1.92	2.99	3.84	4.55	5.03	5.27
Mol % monochloro-acetic acid	68.21	68.21	74.81	84.13	93.20	100.0		
$\kappa \times 10^7$	5.59	15.54	15.64	15.33	14.67	14.1		
		(60°)	(60°)	(60°)	(60°)	(60°)		

Propionic Acid : Acetic Acid.—Propionic acid, with no measurable conductivity, was prepared from a reputed C. P. product by fractional distillation. The results are reproduced in Fig. 3.

Mol % propionic acid.....	0.00	7.51	28.80	54.59	74.63	91.14	100.0
$\kappa \times 10^7$	0.24	0.18	0.13	0.07	0.06	0.03	<0.01

Formamide : Acetic Acid.—The formamide employed had been prepared by heating ammonium formate. The removal of traces of decomposition products formed during this preparation was found to be a matter of extreme difficulty. Partial crystallization did not prove successful,³⁶ but a product of sufficient purity was finally secured by careful fractionation *in vacuo*. The specific conductivity of the best fraction obtained was 4×10^{-6} . The amount of this fraction was too small for making up a complete series of solutions, and the values given below were derived with the use of material of a higher conductivity; $\kappa = 9 \times 10^{-6}$. Previous investigators³⁷ have encountered similar difficulties in the preparation of a standard product and have adopted the same procedure. While the results thus obtained are naturally not so reliable as in the case of other systems, yet for purposes of comparison their degree of accuracy is amply sufficient (see Fig. 3).

Mol % formamide.....	0.00	4.00	11.08	21.05	28.42	36.42	44.74	53.15
$\kappa \times 10^7$	0.24	4.36	33.88	201.4	300.5	380.3	448.1	515.7
Mol % formamide.....	64.48	73.41	80.01	84.11	95.18	100.0		
$\kappa \times 10^7$	629.2	641.8	605.4	515.0	177.2	91.4		

Consideration of Results.

Pure Liquids.—The connection between association and self-ionization in pure liquids, discussed in the preceding article, is typically illustrated by the data presented in Table I. The esters, which are practically non-associated, also exhibit practically zero conductivity. The ketones and acids, with higher degrees of association, possess specific conductivities in general of a higher order. In view of the uncertainty in some of the values,³⁸ this qualitative agreement with theory is all that can be demonstrated here. For strict comparison purposes, moreover, differences in viscosity and ionic mobilities in the various liquids must also be taken into account.

³⁶ Braun, THIS JOURNAL, 40, 793 (1918).

³⁷ Davis and Putnam, *J. Franklin Inst.*, 180, 577 (1915). These investigators find that solutions with formamide as one component show little difference in specific conductivity, whether material of $\kappa = 7 \times 10^{-6}$ or $\kappa = 15 \times 10^{-6}$ is employed.

³⁸ Some of the figures given (*e. g.*, for formamide) are certainly too high. In most cases, however, it is doubtful whether further attempts at purification would lower the specific conductivity appreciably. Such drastic changes in the accepted values as have here been effected are, at any rate, not likely to recur.

Solutions.—The conductivities of the mixtures investigated are, except in such cases where the "diversity factor" is negligible,³⁹ considerably in excess of those of the pure components, as will be evident by inspection of the diagrams. The maxima on the curves are listed below. Where compounds have been isolated by the examination of the freezing-point curve of the system, their formulas and melting points are also indicated. In order to economize space in presenting formulas, the letters A and B are used throughout to indicate the first and second components of each system.

TABLE II.—MAXIMUM SPECIFIC CONDUCTIVITIES OF MIXTURES.

System.	Max. spec. cond. (mhos. $\times 10^7$).	Composition of solution of max. cond. (Mol. % component A).	Com-pounds isolated.	M. p. ($^{\circ}$ C.).
Trichloro-acetic acid: ethyl acetate	10.1	41	AB	—27
Trichloro-acetic acid: ethyl benzoate	8.3	61	AB	—23
Trichloro-acetic acid: benzyl benzoate	0.84	75	AB	+11.9
Acetic acid: ethyl benzoate	0.44	83
Trichloro-acetic acid: acetone	225.0	22
Trichloro-acetic acid: acetophenone	22.6	58	AB	+26
Acetic acid: acetone	5.1	53
Acetic acid: acetophenone	3.6	33
Trichloro-acetic acid: acetic acid	8.3	28
Monochloro-acetic acid: acetic acid	5.6	75
Formamide: acetic acid	646.0	72	AB ₂	⁴⁰ —8

In no case does the position of the maximum point correspond with the composition of the isolable compound, or indeed, except by chance, with *any* simple molecular proportions of the two components. No exact correspondence, however, although frequently sought for by earlier investigators,⁴¹ is to be expected, even under the assumption here made that the conductivity of the mixtures is to be ascribed to the ionic instability of the addition compounds formed. For, in the first place (as may be seen from Table I), considerable changes in viscosity occur in any given system as composition is varied, and such viscosity changes will necessarily be accompanied by variations in the mobilities of the ions. The point of highest ionic concentration is not, in consequence, the point of highest specific conductivity.⁴² A second disturbing factor of equal importance is the change in average ionic complexity with change in composition. Addition compounds other than the equimolecular are certainly present in solutions of the types here studied,⁴³ even although their concentration

³⁹ *E. g.*, in the systems, acetic acid: propionic acid; acetic acid: ethyl acetate.

⁴⁰ English and Turner, *J. Chem. Soc.*, 107, 777 (1915).

⁴¹ For references see Carrara, *Ahrens' Sammlung*, 12, 403 (1908); Dhar, *Z. Elektrochem.*, 20, 57 (1914).

⁴² The viscosity curves of the systems here examined will be presented in a subsequent paper.

⁴³ See Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2305 (1917).

may not be sufficient to permit of their actual isolation. The relative amounts of the various compounds will vary with the solution, each compound (according to the law of mass action) being present in maximum quantity in a solution of its own composition. Each compound, furthermore, will have its own particular "ionic instability," the most simple in type, the equimolecular, being also the least unstable. We can hardly postulate, therefore, a *maximum* specific conductivity for the solution of equimolecular composition when compounds of more complex character, although present in smaller amounts, may exhibit very superior tendencies towards ionic disintegration. In certain cases, indeed, where the equimolecular compound is exceptionally stable and where other compounds, much less stable in comparison, are also formed in quantity, we may expect to find not a maximum but a *minimum* specific conductivity for the equimolecular solution. Actual examples of this type are discussed later.

How far the predicted parallelism between compound formation and ionization is experimentally realized in the systems examined may now be briefly discussed.

Systems of the Type Acid: Ester.—According to the rules outlined in the introduction, solutions of trichloro-acetic acid with ethyl acetate should show the highest conductivities of all those here studied, followed by solutions of the same acid with ethyl benzoate and benzyl benzoate. The three esters with acetic acid should exhibit very much lower conductivities.

Inspection of Fig. 1 and Table II will show that this is the case. At the one extreme we have the system trichloro-acetic acid:ethyl acetate, with a maximum specific conductivity of 10×10^{-7} , at the other extreme the system acetic acid:benzyl benzoate, with conductivities immeasurably small. The only break in the regularity consists in the slight superiority of the system acetic acid:ethyl benzoate over the system acetic acid:ethyl acetate. The conductivities throughout both of these systems, however, are only of the same order as that of pure acetic acid.

Systems of the Type Acid: Ketone.—Employing our theory as before, we may predict here that solutions of trichloro-acetic acid with acetone will possess higher conductivities than those of the same acid with acetophenone, and that the two ketones with acetic acid will give much more poorly conducting solutions. Again the experimental results are in agreement, as may be seen from Fig. 2 and Table II.

The conductivities in this series are very much greater than in corresponding ester systems; for example, the system trichloro-acetic acid:acetone shows a maximum specific conductivity of 225×10^{-7} . This must be ascribed to the "unsaturation factor," discussed in the preceding article,⁴⁴ the ketones being typical associated liquids while the esters are practically non-associated.

⁴⁴ P. 1421.

Systems of the Type Acid : Acid.—While very high conductivities are not to be expected here, yet the large range in the "diversity factor" through the series should be reflected in correspondingly large variations in the specific conductivities obtained. In actual fact, we find the system of two very dissimilar acids trichloro-acetic acid:acetic acid with a maximum value of 8.3×10^{-7} , while the system of two essentially similar acids propionic acid:acetic acid possesses negligible conductivities throughout. The curve for the system monochloro-acetic acid:acetic acid is intermediate in its position.

Systems of the Type Acid : Base.—The increase in the "diversity factor" here results in vastly increased compound formation and specific conductivity in the solutions. Thus even an exceedingly weak base such as formamide gives an isolable addition product with acetic acid, and the maximum specific conductivity exceeds 600×10^{-7} . Water, another very weak base, gives a much more pronounced maximum.⁴⁵ Solutions of stronger bases, such as the substituted alkyl and aryl amines, give still higher conductivities with acetic acid. Our uncertainty as to the actual strengths of such bases renders close comparison difficult, yet it is significant that the order of the maxima obtained by Konovalov⁴⁶ for aniline and its methyl-substituted derivatives with acetic acid parallels the order of the dissociation constants of these bases⁴⁷ in aqueous solution (*i. e.*, methyl aniline > aniline > dimethyl aniline). With the much stronger arylamines (amylamine and *isobutyl* amine) and acetic acid, Patten⁴⁸ obtained specific conductivity curves showing *two distinct maxima*, one on either side of the equimolecular mixture, which thus exhibits a *minimum* conductivity. The diversity between the two components is here, evidently, sufficiently pronounced to induce the formation in quantity of compounds more complex and ionically much more unstable than the simple equimolecular compound. An exactly similar curve is given by a more familiar system of the same type, sulfuric acid:water,⁴⁹ a minimum specific conductivity corresponding with the stable equimolecular compound, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Methyl and ethyl alcohols with hydrogen chloride may be cited as additional examples, already discussed from the same viewpoint by Maass and McIntosh.⁵⁰

Compound Formation and Electro-affinity.

The results of the present article may also be interpreted—reversing for the moment the sequence of the argument—as justifying the tacit assump-

⁴⁵ Rivett and Sidgwick, *J. Chem. Soc.*, 97, 734 (1910).

⁴⁶ Konovalov, *Wied. Ann.*, 49, 733 (1893).

⁴⁷ Landolt-Börnstein, "Tabellen," 1912, p. 1179.

⁴⁸ Patten, *J. Phys. Chem.*, 6, 554 (1902).

⁴⁹ Kohlrausch, Landolt-Börnstein, "Tabellen," 1912, p. 1099.

⁵⁰ Maass and McIntosh, *THIS JOURNAL*, 35, 535 (1913).

tion made throughout this series that the "diversity factor" for the constituent groups in *non-aqueous* solutions may be postulated directly from the results obtained by comparison of acidic (or basic) strengths or by differences in electrode potentials in *aqueous* solutions. It has been demonstrated here, for example, that trichloro-acetic acid is much stronger than acetic acid not only in water, but in other basic solvents such as ketones and esters.⁵¹ When acetic acid is employed as a solvent, an acid of similar strength in aqueous solution (propionic acid) is practically a non-electrolyte, while stronger acids (monochloro-acetic, trichloro-acetic) and bases (formamide, water, aniline, amyl amine) give increasingly greater specific conductivities the greater the divergence in character exhibited by the variable group in aqueous solutions.⁵² We can therefore deduce the general rules that the order of the electro-affinities of different radicals is substantially the same whatever the solvent, and that increasing diversity in the electro-affinities of the constituent groups runs parallel to association in pure liquids, to compound formation in binary solutions, and to ionization in both.⁵³

Summary.

The complete specific-conductivity—composition curves for 14 systems of the types: acid: ester, acid: ketone, acid: acid and acid: base have been determined with the greatest possible degree of accuracy. New standards of purity (as demonstrated by lowering of accepted specific-conductivity values) have been set for the majority of the substances employed.

The conductivities of solutions of the above types are, in general, considerably in excess of those of the pure components, and increase uniformly with increasing diversity in character (*i. e.*, in the positive or negative nature of the constituent radicals) of their components. The results here obtained have been correlated with those derived from freezing-point measurements upon similar systems, and the validity of the fundamental relationships between compound formation and ionization in solutions, postulated in the preceding article, has been confirmed.

In subsequent papers the viscosity curves for the above systems will be presented and the theoretical discussion continued.

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⁵¹ See also Walker, McIntosh and Archibald, *J. Chem. Soc.*, **85**, 1098 (1904).

⁵² See also Walden, *Trans. Faraday Soc.*, **6**, 71 (1910).

⁵³ Compare Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921). Apparent exceptions to these rules will be noted and discussed in a subsequent paper.