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THE CONDUCTIVITY AND IONIZATION OF A PENTA- AND A HEXA-IONIC SALT.

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1. Purpose of the Investigation.

A study of the existing conductivity data relating to salts of poly-ionic, multivalent types has led to the conclusion that the change of the ionization (γ) of such salts (as derived from the conductance-ratio Λ/Λ_0) with the concentration (C) may be expressed by the same function as holds true in the case of uni-univalent salts, in spite of the fact that the mass-action law requires a different function.[1] Thus the function $C(1-\gamma) = K(C\gamma)^n$ holds true approximately for almost all salts of whatever type investigated, when to the exponent n are given values which vary only between the limits of 1.40 and 1.55, although the mass-action law requires a value of n equal to the number of ions into which the salt dissociates—thus 2 for di-ionic salts, 3 for tri-ionic salts, etc. The further conclusions have also been drawn, (1) that the degree of ionization (γ) at a given (small) concentration is not far from the same for almost all salts of the same type,

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[1] See This Journal, 30, 343 (1908); 31, 1000 (1909).

and (2) that the un-ionized fraction $(1 - \gamma)$ at any definit (small) molal concentration is roughly proportional, in the case of different types of salts, to the product of the valences v_1, v_2 of the two ions of the salt;[1] that is, $(1 - \gamma) = K(v_1 v_2)$ for a definit value of C, K having a value of about 0.13 at 0.05 molal at 18° or 25°.

The number of the salts yielding more than three ions that have been accurately investigated in these directions is, however, very small.[2] This investigation was therefore undertaken, with the aid of a grant from the Carnegie Institution of Washington, in order to test further the applicability of these principles in the case of salts of high valence types. Two salts, with valence-products 1×5 and 1×4, respectively, were employed; namely the penta- and tetra-sodium salts of benzene-pentacarboxylic acid, $C_6H(COOH)_5$. Incidentally the conductance of the acid itself was also measured.

The conductance of the two salts were measured at 0°, 25°, and 50° at the concentrations 0.2, 0.6, 2, 6, 20, and 50 milliformal.[3] The conductances of the acid were measured only at 25°, at the concentrations 0.6 to 20 milliformal. In addition to the conductance measurements, the viscosities of the salt solutions were determined. From these conductance and viscosity data the ionization (γ) of the salts was calculated by means of the equation $\gamma = \mu\eta/\mu_0\eta_0$ in which η and η_0 are the viscosities of the solution and of pure water, and μ and μ_0 are the formal conductances at the concentration in question and at zero concentration, respectively.

The density of all solutions was also determined, in order to compute the volume concentration of the solutions from their composition by weight, since for greater convenience and accuracy they were all made up by weighing.

Incidentally it was also necessary to make sure that the degree of hydrolysis of the penta-sodium salt and the hydrogen ionization of the tetra-sodium salt were not large enough to influence appreciably the conductance. This was done by the use of phenolphthalein and paranitro-

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[1] THIS JOURNAL, 30, 348 (1908); 31, 1003 (1909).

[2] Noyes and Johnston (THIS JOURNAL, 31, 997–1006 (1909)) studied at temperatures from 0° to 100° or above, potassium citrate and lanthanum nitrate as examples of the uni-trivalent type, potassium ferrocyanide as an example of the uni-quadrivalent type, and barium ferrocyanide, calcium ferrocyanide, and lanthanum sulfate as examples of still higher types. Whetham (*Z. physik. Chem.*, 33, 351 (1900)) studied potassium ferricyanide at 0° up to 0.01 normal. Ostwald (*Ibid.*, 2, 903 (1888)) and Walden (*Ibid.*, 8, 446 (1891)) have investigated at 25° the sodium salts of several polybasic organic acids.

[3] Concentrations expressed in formula weights per liter are designated throughout this article as *formal concentrations*, in accordance with the practice followed in this laboratory.

phenol respectively, with the aid of the theory of indicators.[1] It was estimated in this way that at 25° the hydroxyl-ion concentration in a 0.02 formal solution of the penta-sodium salt prepared, like that used for the measurements, by titrating the acid with sodium hydroxide with phenolphthalein to a faint red color was 2×10^{-7}; and that the hydrogen-ion concentration in a 0.02 formal solution of the tetra-sodium salt is 3×10^{-6} mols per liter. The hydrogen-ion concentration in solutions of the tetra-sodium salt at 25° was estimated to be 3×10^{-6} mols per liter at all concentrations.[2] Neither of these quantities is large enough to give rise to a conductance forming an important part of the total conductance, even in the case of the most dilute solutions investigated.

2. Description of the Conductivity Apparatus and Method.

Conductivity Apparatus.—The conductances at all three temperatures were measured in two glass cells of the pipet type.[3] Cell "A" was designed for measuring concentrated solutions and was used for the concentrations above 2 milliformal. Cell "B" was designed and used for the solutions at or below 2 milliformal.

The conductances were measured on a slide-wire bridge of the roller type.[4] The slide wire was calibrated both by the method of Strouhal and Barus,[5] and by the use of resistance boxes.[6] The resistance coils of the bridge were also calibrated. The resistance of the leads, which

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[1] See THIS JOURNAL, 32, 820 (1909).

[2] The estimates were based on the following experiments: 10 cc. of a paranitrophenol solution were added to 70 cc. of a 0.022 formal solution of the tetra-sodium salt, Na_4HA, and the volume of the same paranitrophenol solution which had to be added to 80 cc. of dilute NaOH to give the same color was determined. This volume was found to be 0.30 cc., showing that the indicator was 3.0% transformed into its colored salt in the solution of the salt. From this we find, taking the constant K_I of the indicator-acid (HIn) as 9×10^{-8}, $C_{H^+} = K_I \frac{C_{HIn}}{C_{In}} = 9 \times 10^{-8} \times \frac{97.0}{3.0} = 2.9 \times 10^{-6}$. Entirely similar experiments were made with 0.022 formal solutions of $(0.97\, Na_4HA + 0.03 Na_3H_2A)$ and of $(0.97 Na_4HA + 0.03 Na_5A)$. In the former of these solutions the fraction of the indicator transformed was found to be 2.6%, from which C_{H^+} is calculated to be 3.4×10^{-6}. In the latter solution the fraction transformed was found to be 3.4%, from which follows $C_{H^+} = 2.5 \times 10^{-6}$. The experiments with the penta-sodium salt were made with phenolphthalein in a similar way. The addition of enough NaOH to correspond to $Na_5A + 0.01 NaOH$ only increased C_{OH^-} from 2×10^{-7} to 1×10^{-6}. It is to be noted that the solutions tested were those prepared by titration and did not contain exactly equivalent quantities of sodium and the acid constituent

[3] THIS JOURNAL, 31, 732 (1909).

[4] Kohlrausch and Holborn, *Das Leitvermögen der Elektrolyte*, pp. 41–42.

[5] Ostwald-Luther, *Phys. Chem. Messungen.*, 3rd Ed., p. 408 (1910).

[6] *Loc. cit.*, p. 407.

was 0.036 ohm in the 0° and 50° measurements and 0.021 in the 25° measurements, was corrected for.

Thermostats.—The 0° bath was a well-lagged cylindrical metal vessel filled with a mixture of distilled water and a large proportion of crushed ice. It was not found necessary to stir it, as its temperature remained constant within 0.02°. At 25° and 50° electrically heated thermostats, provided with efficient stirrers, were used. The variations of temperature from 25° or 50° never exceeded 0.02°.

Thermometers.—Three thermometers, graduated in tenths of a degree, were used—one for each of the three temperatures. They were calibrated, in the position in which they were used, by comparison with a standard Baudin thermometer which had been certified by the Bureau of Standards at Washington.

Conductance-Capacity of the Cells.—The conductance-capacities of both the cells were determined by measuring in them the conductance at 18° of a 0.01 normal potassium chloride solution, freshly prepared by dissolving, in accordance to the specifications of Kohlrausch,[1] 0.7456 g. (weighed in air) of recrystallized potassium chloride in one liter of solution at 18°. The specific conductance of this solution was taken as 0.0012243.[2]

The conductance-capacity was determined before and after each series of dilutions of a solution, eleven times in all. The values remained constant within 0.1 per cent. throughout the work. Those used were 4.393 for cell "A" and 0.07670 for the cell "B."

The Water Correction.—The specific conductance of the water from which the more dilute solutions were prepared was measured at 25° and subtracted from that of the solution. The average values in reciprocal ohms of the specific conductance of the water (after it had been shaken in the bottle in which the solution was to be made) are as follows: 0.4×10^{-6} at 0°; 0.8×10^{-6} at 25°; and 1.2×10^{-6} at 50°. The percentage correction was very small, except in the case of the 0.0006 formal salt solution, where it amounted to 0.2 to 0.3 per cent. and in the case of the 0.0002 formal solutions where it amounted to 0.4 to 0.7 per cent.

Procedure.—The measurements at 0°, 25°, and 50° were always made in this order in immediate succession, with the same filling of the cell. After the 50° measurement, the solution was brought back to 25° and then to 0°, and again measured at these temperatures. The return values were usually identical with the original values, the only exception observed being that the conductance of the 0.0002 formal solution of the penta-sodium salt was 0.1 per cent. to 0.2 per cent. larger after

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[1] *Wissen. Abhd. Phys.-techn. Reichsanstalt,* **3**, 180 (1900).

[2] *Loc. cit.*, p. 210.

the solution had been heated to 50°. The conductance of the solutions was usually measured on the day after they were prepared.

3. Preparation of the Substances and Solutions.

Benzenepentacarboxylic Acid.—The benzenepentacarboxylic acid used in this investigation was furnished us by Professor John E. Bucher, of Brown University, for which we wish to express to him our great indebtedness. It was prepared by him by a process of which he will later publish a description. It had been recrystallized three times from cold water, and then had been dried to constant weight in a room at 5°. This treatment was to assure the production of the penta-hydrate, $C_6H(COOH)_5.5H_2O$. He found by titration, using phenolphthalein as an indicator, a molecular weight of 388.1, the theory for $C_6H(COOH)_5.5H_2O$ being also 388.1. He states also that heating at about 95° in a steam-heated Victor Meyer bath caused a loss of weight of 23.16 per cent., the water content calculated from the above formula being 23.21 per cent.

As a stock solution from which all other solutions were made, there were prepared about 250 cc. of an approximately 0.1 formal solution of the acid. For this purpose a portion of the acid was dried to constant weight at 130°, was accurately weighed, and was then washed into a weighed 250 cc. "Resistenz-Glas"[1] bottle with approximately the desired volume of conductivity water, and the bottle and solution were weighed. The concentration of this solution was computed to be 0.5551 equivalents of acid per 1000 grams of solution. Three titrations against a standard (approximately 0.1 normal) solution of Merck's sodium hydroxide with phenolphthalein gave the values 0.5540, 0.5540, and 0.5544 equivalent per 1000 grams of solution. The mean value 0.5546 was employed as the basis of the concentrations of the acid solutions whose conductance was measured.

A portion of this stock acid solution was diluted to a concentration of 0.1 equivalent of acid per 1000 grams of solution. From this solution the three more dilute solutions whose conductance was measured were prepared by weighing a portion of the stock solution into a carefully cleaned "Resistenz-Glas" bottle, adding the calculated weight of conductivity water and weighing again. Duplicate solutions were prepared in all cases, except for the conductance measurements with the 0.05 formal solutions of the salts and the 0.02 formal solution of the acid, and for the viscosity measurements with the salts.

All the standard sodium hydroxide solutions used in the work were titrated against a hydrochloric acid solution, the strength of which had been determined gravimetrically by precipitation as silver chloride.

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[1] These bottles, made by Greiner and Friedrich, of Stützerbach, Germany, were used throughout the work.

The international atomic weights of 1911 were used throughout the work. Weights were not reduced to the vacuum standard.

Penta-sodium Benzenepentacarboxylate.—This salt was prepared in solution by exactly neutralizing with the aid of phenolphthalein[1] a portion of the stock solution of the acid with a standard (approximately 0.6 normal) solution of sodium hydroxide, prepared as described below. This stock solution of the penta-sodium salt was diluted, by weight, first to 0.05 formal, and then to 0.02 formal; and from this last solution all the other more dilute solutions were made.

Tetra-sodium Benzenepentacarboxylate.—The tetra-sodium salt was made in solution by adding to a weighed portion of the stock solution of the acid, contained in a 250 cc. bottle, 80 per cent. of the weight of freshly prepared standard sodium hydroxide solution found to be necessary for complete neutralization. The solution was diluted as in the case of the penta-sodium salt.

Sodium Hydroxide Solutions.—In order to eliminate carbonate, the sodium hydroxide solutions used for making the sodium salts of the acid were prepared by decomposing with water electrolytically prepared sodium amalgam. In detail the process was as follows: About 200 cc. of a saturated solution of pure sodium carbonate were electrolyzed with a current of 0.5 ampere for about 48 hours in a 300 cc. separatory funnel surrounded with ice and containing 60–100 cc. of pure mercury as cathode and a platinum wire as anode. The amalgam was then allowed to run slowly into a 500 cc. bottle (filled with air free from carbon dioxide), provided with a soda-lime tube and a delivery tube. Fresh conductivity water was then forced into it through the delivery tube. A platinum tube standing upright in the amalgam served to accelerate its decomposition, which is otherwise slow at room temperature. The first sodium hydroxide solution, from which was made the solution of the penta-sodium salt used in the conductivity work, developed, after standing, a very slight turbidity, which was apparently due to the bottle having been attacked by the solution. Therefore, in making the later solutions, the interior of the bottle was coated (at 225°) with paraffin which had been filtered, boiled with sodium hydroxide solution, and then washed with hot water until free from alkali. Altogether, three solutions were made by this method, one for the conductance measurements with the penta-sodium, and one for those with the tetra-sodium salt, and a third for the viscosity measurements with both salts.

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[1] Only 0.05 cc. of the phenolphthalein solution was used, and this had been especially prepared by dissolving 0.2 g. purified phenolphthalein in 50 cc. of a 50 per cent. mixture of conductivity water and pure alcohol. Four drops of this solution increased the specific conductance of conductivity water only from 0.8×10^{-6} to 1.2×10^{-6} so that its effect upon the conductance of the solutions was negligible.

4. The Densities and Volume-Concentrations of the Solutions.

The densities of the solutions, which were determined in a Sprengel-Ostwald 10 cc. picnometer, are given in Table I. The values are ratios of the densities to that of water at 4°. The numbers in the first column show the number of milliformula-weights per 1000 grams of solution.

TABLE I.—DENSITIES OF THE SOLUTIONS.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°.	Penta salt at 25°.	Tetra salt at 25°.	Penta salt at 50°.	Tetra salt at 50°.
50	1.0172	1.0152	......	1.0136	1.0116	1.0041	1.0019
20	1.0067	1.0060	1.0000	1.0037	1.0029	0.99440	0.99369
6	1.0020	1.0017	0.99804	0.99910	0.99890	0.99002	0.98978
2	1.0006	1.0005	0.99740	0.99781	0.99772	0.98871	0.98864
0	0.99987	0.99987	0.99707	0.99707	0.99707	0.98807	0.98807

Table II contains in the last seven columns the values of the volume-concentrations, expressed in milliformula-weights per 1000 cc. of solution, computed from the densities and the compositions by weight given in Table I and in the first column of Table II:

TABLE II.—FORMAL CONCENTRATIONS CORRESPONDING TO COMPOSITIONS BY WEIGHT.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°.	Penta salt at 25°.	Tetra salt at 25°.	Penta salt at 50°.	Tetra salt at 50°.
50.0	50.86	50.76	....	50.68	50.58	50.21	50.11
20.0	20.14	20.12	20.00	20.08	20.06	19.89	19.87
6.0	6.012	6.010	5.988	5.994	5.994	5.940	5.938
2.0	2.002	2.002	1.995	1.996	1.995	1.977	1.977
0.6	0.6000	0.5998	0.5982	0.5982	0.5982	0.5928	0.5928
0.2	0.2000	0.2000	....	0.1994	0.1994	0.1976	0.1976

5. The Specific Conductance Data.

Table III contains the values of the specific conductance in reciprocal ohms. In deriving these values, the conductance of the solution meas-

TABLE III.—SPECIFIC CONDUCTANCE × 10^4.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°.	Penta salt at 25°.	Tetra salt at 25°.	Penta salt at 50°.	Tetra salt at 50°
50.0	71.62	61.31	...	140.8	121.2	218.3	190.3
20.0	33.92	28.79	55.21	66.14	56.54	102.1	88.65
	33.92	28.81	...	66.11	56.54	102.2	88.61
6.0	12.57	10.44	22.70	24.40	20.41	37.78	32.07
	12.56	10.44	22.72	24.39	20.41	37.75	32.07
2.0	5.022	4.029	9.681	9.761	7.904	15.17	12.46
	5.020	4.029	9.689	9.765	7.908	15.17	12.45
0.6	1.773	1.364	3.674	3.456	2.684	5.427	4.253
	1.774	1.364	3.670	3.457	2.684	5.427	4.254
0.2	0.6475[1]	0.4900	.....	1.270[1]	0.9636	2.004[1]	1.532
	0.6518	0.4899	.....	1.276	0.9633	2.017	1.532
	0.6496	.....	.....	1.276	.....	2.017	.....
	.....	.....	.....	1.276	.....	.....	.....

[1] These values were rejected in deriving the final value.

ured in the cell (corrected for errors in the bridge and for the resistance of the leads) was multiplied by the conductance-capacity of the cell, and from this product the specific conductance of the water was subtracted. When more than one value is given at a concentration, it represents the results from two or more independently prepared solutions. The general agreement between such results shows that the conductance measurements were reproducible within 0.1 per cent. except in the case of the 0.0002 formal solutions, where the large water correction and the sensitiveness of contamination make the results uncertain by 0.2–0.3 per cent.

6. Values of the Formal Conductance.

The formal conductance[1] (μ) at each concentration and temperature was obtained by dividing the average of the specific conductance values $\times 10^4$ given in Table III by 10 times the corresponding formal concentration given in Table II.

The formal conductance (μ_0) at zero concentration was computed by the method usually employed in this laboratory;[2] namely, by plotting $1/\mu$ against $(C\mu)^{n-1}$ with various values of the exponent n and extrapolating to zero concentration by means of the curve that is most nearly a straight line at the three smallest concentrations.

The values of the formal conductance obtained in this way are given in Table IV:

TABLE IV.—VALUES OF THE FORMAL CONDUCTANCE.

Comp. by wt.	Penta salt at 0°.	Tetra salt at 0°.	Acid at 25°.	Penta salt at 25°.	Tetra salt at 25°.	Penta salt at 50°.	Tetra salt at 50°.
50.0	140.8	120.8	...	277.9	239.6	434.8	379.9
20.0	168.5	143.2	276.1	329.5	281.9	508.0	446.0
6.0	209.1	173.7	379.2	407.0	340.6	636.0	540.0
2.0	251.0	201.4	485.5	489.3	396.3	767.0	630.0
0.6	295.7	227.4	614.0	578.0	448.7	915.5	717.5
0.2	325.4	245.1	...	640.0	483.2	1020.5	775.0
0.0	371	276	...	751	536	1222	868

7. Relative Values of the Conductances of the Two Anions.

By subtracting from the formal conductances of the penta-sodium and tetra-sodium salts at zero concentration the conductance of five and four equivalents of sodium-ion[3] respectively, the following values are obtained for the formal conductance of the ions $(C_{11}HO_{10})^{V}$ and $(C_{11}H_2O_{10})^{IV}$.

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[1] By "formal conductance" is meant the conductance between electrodes one centimeter apart of that quantity of the solution which contains one formula-weight of the salt.

[2] See Noyes and Johnston, THIS JOURNAL, 31, 994 (1909).

[3] The equivalent conductance of sodium-ion being taken, in accordance with the calculations of Johnston (THIS JOURNAL, 31, 1015 (1909)), as 26 at 0°, 51 at 25°, and 82 at 50°.

	0°.	25°.	50°.
$(C_{11}HO_{10})^{V}$	241	496	812
$(C_{11}H_2O_{10})^{IV}$	172	332	540
Ratio	1.40	1.49	1.50

Since these two ions differ in molecular composition by only one hydrogen atom, it might be expected (assuming equal hydration) that they would meet with nearly the same frictional resistance to their motion through the solution. Their linear velocities would then be proportional to the electric force acting upon them and therefore to the charge upon them, so that the ratio of their velocities would be 5 : 4. Since the relative quantities of electricity transported by one formula-weight of the two ions are also as 5 : 4, the ratio of their formal conductances would be $5^2 : 4^2$ or 1.56. This is in fact not very different from the actual values of the ratios at 25° and 50°. Similar relations were found to hold true by Abbott and Bray[1] for the ions of phosphoric acid and of pyrophosphoric acid.

8. The Ionization Relations of Benzenepentacarboxylic Acid.

An idea of the ionization relations of the benzenepentacarboxylic acid at 25° may be obtained by comparing its formal conductances given in Table IV for the various concentrations with the conductance values that would correspond to complete ionization of the first hydrogen and of the second hydrogen of the acid. These latter values (taking μ for $H^+ = 350$, μ for $C_{11}H_5O_{10}^- = 21$, and μ for $C_{11}H_4O_{10}^{=} = 84$) are 371 and 784, respectively. It will be seen that the actual conductance at 0.006 formal corresponds approximately with that for complete ionization of the first hydrogen, and that that at 0.0006 formal is nearly 80 per cent. of that corresponding to complete ionization of two hydrogens. These results show therefore that the acid remains a fairly strong one until at least two of its five hydrogens have been neutralized by a base.[2]

9. The Viscosity Measurements.

Apparatus and Method.—The viscosities of the solutions were measured in a viscosimeter, similar to that described by Ostwald and Luther.[3] The volume of the upper bulb was about 13 cc. and the diameter and length of the capillary tube were 0.052 and 20 cm., respectively. The time of flow of water at 25° was 514 seconds.[4]

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[1] THIS JOURNAL, **31**, 762 (1909).

[2] It may be incidentally mentioned that the change of conductance of the acid between the concentrations studied (0.0006 to 0.02 formal) is satisfactorily expressed by the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^{1.50}$, Λ_0 being considered merely as an arbitrary empirical constant.

[3] *Phys.-Chem. Messungen*, 3rd Ed., p. 231 (1910).

[4] For a capillary tube of these dimensions, the limiting velocity of flow, which cannot be exceeded without introducing an error of 0.1 per cent., due to the eddying of the liquid in the capillary, is, according to a formula deduced by Grüneisen (*Wissens.*

The viscosimeter was wired firmly to a vulcanite plate, which was supported from the side of the thermostat through a ball-and-socket joint, and was therefore capable of adjustment in all directions. A plummet attached to the vulcanite plate made it possible to bring the viscosimeter always to exactly the same vertical position. The viscosimeter was filled from a 25 cc. pipet, into which the solution had been forced through a small asbestos filter, which removed any particles suspended in the solution. The time of flow was measured by a stop-watch with a dial divided into fifths of a second, nine to sixteen check measurements being made with each filling.

The Viscosity Data.—In Table V are presented the results of the viscosity measurements. The first column contains the composition of the solution by weight, expressed in milliformula-weights per 1000 grams of solution. The second column contains the time of flow in seconds; and the third, the average deviation of the individual values from the means. In the fourth column are given separate values (corresponding to different fillings of the apparatus with the same solution), and in the fifth column average values of the ratio (η/η_0) of the viscosity of the solution to that of water at the same temperature. These values were computed by the formula $\eta/\eta_0 = td/t_0d_0$, where d and d_0 are the densities

TABLE V.—THE VISCOSITY DATA.

Tetra-sodium Salt.

				Viscosity-ratio.	
Temp.	Comp. by wt.	Time of flow.	a. d.	Separate values.	Mean value.
25°	50.0	546.08	±0.30	1.0772	1.0772
	20.0	529.01	±0.35	1.0345	
		528.49	±0.56	1.0335	1.0340
	6.0	519.86	±0.43	1.0117	
		519.93	±0.37	1.0118	1.0118
	2.0	517.17	±0.38	1.0063	
		516.08	±0.22	1.0042	1.0053
	0.6	516.13	±0.32	1.0035	
		515.32	±0.60	1.0019	1.0027
	0.0	514.34[1]	±0.27	1.0000	1.0000
0°	50.0	1091.2	±0.6	1.0762	1.0762
	20.0	1055.7	±0.3	1.0317	1.0317
	0.0	1029.5	±0.6	1.0000	1.0000
50°	50.0	341.18	±0.38	1.0767	1.0767
	0.0	321.30	±0.26	1.0000	1.0000

Abh. Phys.-Techn. Reichsanstalt, 4, 165 (1904)) 20 centimeters per second—thus much larger than that in our experiments, which was 12 centimeters per second. The accuracy of the viscosimeter was also tested by measuring in it, at 18°, the velocity of a normal sodium chloride solution, the value being found to agree with that given by Grüneisen within 0.1 per cent.

[1] Mean of five measurements.

TABLE V (*Continued*).
Penta-sodium Salt.

Temp.	Comp. by wt.	Time of flow.	a. d.	Viscosity-ratio. Separate values.	Viscosity-ratio. Mean value.
25°	50.0	551.34	±0.37	1.0897	1.0897
	20.0	530.27	±0.26	1.0378	
		530.68	±0.22	1.0386	1.0382
	6.0	520.89	±0.48	1.0148	
		520.94	±0.40	1.0149	1.0149
	2.0	516.49	±0.46	1.0049	
		517.16	±0.34	1.0062	1.0056
	0.6	515.79	±0.30	1.0028	
		516.12	±0.22	1.0035	1.0031
	0.0	514.34[1]	±0.27	1.0000	1.0000
0°	50.0	1099.7	±0.6	1.0867	1.0867
	0.0	1029.5	±0.6	1.0000	1.0000
50°	50.0	343.81	±0.19	1.0874	1.0874
	0.0	321.30	±0.26	1.0000	1.0000

of the solution and of water, as given in Table I, and t and t_0 are the times of flow of the solution and of water, respectively.

10. Values for the Ionization of the Two Salts.

From the values of the formal conductance (μ) given in Table IV and of the viscosity (η) given in Table V, the values of the ratio $\mu\eta/\mu_0\eta_0$ for the two salts were calculated.[2] This ratio will be called the ionization (γ); but it should be noted that it is a true measure of ionization only on the assumption that the intermediate ions do not exist. The values so obtained are given in Table VI:

TABLE VI.—IONIZATION VALUES.

Comp. by wt.	0°. Penta salt.	0°. Tetra salt.	25°. Penta salt.	25°. Tetra salt.	50°. Penta salt.	50°. Tetra salt.
50.0	41.3	47.0	40.3	48.1	38.7	47.1
20.0	47.2	53.4	45.6	54.3	43.1	53.1
6.0	57.2	63.6	55.0	64.2	52.8	62.9
2.0	68.1	73.2	65.5	74.2	63.1	72.9
0.6	80.0	82.5	77.2	83.9	75.1	82.9
0.2	87.8	88.7	85.2	90.1	83.5	89.3
0.0	100.0	100.0	100.0	100.0	100.0	100.0

11. Change of Ionization with the Concentration and Temperature.

In order to determine how the ionization (γ) of these salts varies with the concentration, values of $1/\gamma$ were plotted against $(C\gamma)^{n-1}$ with values of n varying between 1.20 and 1.55 inclusive. It was found that with any one value of the exponent the graph was approximately linear

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[1] Mean of five measurements.

[2] At 0° and 50° the viscosity-ratio was taken the same as at 25° except for the stronger solutions with which direct measurements were made at 0° and 50°.

only through a definit interval of concentrations, showing that no exponential function of the form $C(1-\gamma) = K(C\gamma)^n$ satisfactorily expresses the change of ionization with the concentration. The value of the exponent n at 25° giving a linear graph for the concentration-intervals 0.2 to 2.0 milliformal is 1.55 for both salts, and that for the concentration-interval 2 to 20 milliformal is 1.20 for both salts. The value for the lower concentration-interval is about the same as that previously found for uni-uni-, uni-bi-, and uni-trivalent salts;[1] and the decrease of the exponent with increasing concentration conforms also with that commonly shown by salts of lower valence types.[2] This shows that the principle that the form of the functional relation between ionization and concentration is the same whatever be the number of ions into which the salt dissociates is applicable even to these penta- and hexa-ionic salts of the uni-quadrivalent and uni-quinquivalent types.

In considering the effect of temperature on the ionization, it is best, owing to the considerable uncertainty in the μ_0 values obtained by extrapolation, to compare not the ratio $\mu\eta/\mu_0\eta_0$ (of which the values are given in Table VI), but the ratios $\mu\eta/\mu_{0.2}\eta_{0.2}$ (equal to $\gamma/\gamma_{0.2}$) of the ionization at any higher concentration to that at 0.2 milliformal, since these do not involve the μ_0 values. The values of these ratios at the three temperatures for the concentrations 50 and 20 milliformal are as follows:

	Tetra-sodium salt.		Penta-sodium salt.	
	$\gamma_{50}/\gamma_{0.2}$.	$\gamma_{20}/\gamma_{0.2}$.	$\gamma_{50}/\gamma_{0.2}$.	$\gamma_{20}/\gamma_{0.2}$.
0°..............	53.1	60.2	47.0	53.7
25°..............	53.4	60.3	47.3	53.5
50°..............	52.8	59.5	46.3	51.7

It will be seen from the table that the change of the ionization with the temperature is so small as scarcely to exceed the possible experimental errors. There seeems, however, to be a slight decrease between 25° and 50° in the case of both salts.

12. Ionization in Relation to Valence Type.

One other salt of the uni-quadrivalent type, potassium ferrocyanide, has been accurately investigated.[3] It is therefore of interest to compare its ionization with that of the tetra-sodium salt considered in this article.

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[1] Noyes and Johnston, THIS JOURNAL, 31, 1000 (1909).

[2] *Cf.* Abbott and Bray, *Ibid.*, 31, 746 (1909). This change in the exponent will be fully discussed in an article from this laboratory, soon to be published by Noyes and Falk.

[3] Conductance data for this salt were obtained by Noyes and Johnston (*loc. cit.*); viscosity data, by Wagner (*Z. physik. Chem.*, 5, 37 (1890)). The tetra- and penta-sodium salts of certain organic acids were measured by Ostwald (*Z. physik. Chem.*, 2, 903 (1888)) and by Walden (*Ibid.*, 8, 446 (1891)). but no special effort was made to derive an accurate conductance value at zero concentration.

The ionization values at 25° (corrected for viscosity) of the two salts are as follows, those for the tetra-sodium salt having been derived from those in Table VI by graphical interpolation.

Formal conc.	$3\frac{1}{8}$.	$12\frac{1}{2}$.	25.	50.
K_4FeCN_6	71.2	59.0	53.6	49.6
$Na_4C_{11}H_2O_{10}$	70.1	57.9	52.8	48.2

It will be seen that these two very different salts have substantially the same ionization-values, thus confirming the principle that salts of the same valence type have in general approximately the same degree of ionization at the same concentration.

Another purpose of this investigation was to determine whether the principle that the fraction of a salt existing in the un-ionized state at any given molal concentration is roughly proportional to the product of the valences of its ions is applicable also to salts of high valence product, such as those involved in this research. This is shown to be the case by the following table, which gives the un-ionized fraction ($1-\gamma$) at 25° when the salt is 0.05 formal, and the ratio of this fraction to the valence-product (v_1v_2), for these two salts (in the columns headed 4×1 and 5×1) and for the groups of salts of smaller valence-product considered in the article of Noyes and Johnston:

TABLE VII.—UN-IONIZED FRACTION IN RELATION TO VALENCE-PRODUCT.

v_2v_2.	1x1.	2x1.	3x1.	4x1.	5x1.	2x2.
$1-\gamma$	$0.13\frac{1}{2}$	0.28	0.39	0.52	0.60	0.58[1]
$(1-\gamma)/v_1v_2$	$0.13\frac{1}{2}$	0.14	0.13	0.13	0.12	$0.14\frac{1}{2}$

13. Summary.

In this article have been presented the results of measurements at 0°, 25°, and 50° of the formal (molal) conductance (μ), viscosity (η), and density of dilute solutions of the tetra-sodium and penta-sodium salts of benzenepentacarboxylic acid; also values of their conductance (μ_0) at zero concentration obtained by graphical extrapolation, and values (calculated from these data) of the ratio $\mu\eta/\mu_0\eta_0$, which expresses the ionization (γ) of the salts, if it be assumed that intermediate ions are not present.

The following principles, which had been previously derived from the study of salts of smaller valence-products, have been here shown to be applicable also to these two salts:

1. If the change of ionization with the concentration be expressed by a function of the form $C(1-\gamma) = K(C\gamma)^n$, it is found that the exponent n has approximately the same value (1.50 ± 0.05 at concentrations below 0.02 normal), whatever be the number of ions into which the salt dissociates, instead of a value equal to this number of ions, as would be required by the mass-action law. Moreover, as has been found with the salts of smaller valence-product, the value that has to be given

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[1] This value is the average one for the sulfates of magnesium, zinc, and copper.

to the exponent n is smaller at higher concentrations; thus it is 1.20 for these two salts for the concentration interval 0.01 to 0.1 normal.

2. The ionization of different salts of the same valence type is roughly the same at the same concentration. Thus that of the tetra-sodium salt has been shown to be substantially identical with that of potassium ferrocyanide, the other uni-quadrivalent salt that has been accurately investigated.

3. The un-ionized fraction of salts at a given formal (molal) concentration is roughly proportional to the product of the valences of their ions; thus at 0.05 formal the un-ionized fraction is $4 \times 13 = 52$ per cent. for the tetra-sodium salt, and $5 \times 12 = 60$ per cent. for the penta-sodium salt, while the average values previously obtained are $13^1/_2$ for uni-univalent, 2×14 for uni-bivalent, and 3×13 for uni-trivalent salts.

4. Increase of temperature causes only a slight decrease in the ionization of salts. Thus with these two salts the change between 0° and 25° is scarcely appreciable, and that between 25° and 50° amounts at 0.05 formal to 1.5 to 2 per cent. of the ionization value.

In addition, it is shown that at 25 and 50° the molal conductance of the quinquivalent ion $(C_{11}HO_{10})^V$ is 1.5 times that of the quadrivalent ion $C_{11}H_2O_{10}{}^{IV}$, while if these ions encountered the same frictional resistance the larger charge on the former ion would cause its molal conductance to be $5^2/4^2$ or 1.56 times that of the latter ion.

The conductance of benzenepentacarboxylic acid itself was also studied at 25° at the concentrations 0.0006 to 0.02 formal. The results show that it is a moderately strong acid with respect to both its first and second hydrogens.

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THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. II. ELECTRICAL TRANSFERENCE NUMBERS.

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Introduction.

In a previous article[1] was presented the first part of a systematic critical study of the existing data relating to the properties of aqueous salt solutions, interpreted with reference to the Ionic Theory. This article de-

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[1] THIS JOURNAL, **32**, 1011–1030 (1910).