the field of force midway between that of a positive and that of a negative element. The latter view would be in harmony with a continuous transition from the strongly electropositive to the strongly electronegative elements.

This paper can only suggest a few of the applications of the electroatomic theory of valence. It has been interesting to see the development of the theory during the past six years, to note its constant increase in scope and its ability to harmonize the most varied and complex phenomena in widely separated fields of science. In conclusion it may be said that none of the hypotheses here advanced claims acceptance without further verification. The aim of the theory is to develop gradually a precise and exact conception, which shall meet the fundamental needs of both physicists and chemists, and this end can be attained only by the earnest and critical coöperation of all investigators.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

CONDUCTIVITY AND DISSOCIATION OF SOME RATHER UNUSUAL SALTS IN AQUEOUS SOLUTION.[1]

BY CHARLES WATKINS AND HARRY C. JONES.

Received May 29, 1915.

This investigation is a study of the conductivity, temperature coefficients of conductivity and dissociation of electrolytes in aqueous solution. It is a continuation of work begun in this laboratory in 1905,[2] and which has been continued almost without interruption up to the present.

During the past ten years the following investigations bearing on this general problem have been carried out: Jones and Jacobson,[3] Jones and White,[4] Jones and Clover,[5] Jones and West,[6] Jones and Wightman,[7] Jones and Hosford,[8] Jones and Winston,[9] Jones and Wightman,[10] Jones and Springer,[11] Jones and Smith,[12] Jones and Howard,[13] and Jones and

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[1] The results of this investigation will appear in full in *Publ. Carnegie Inst. Wash.*, No. **230** (1915).

[2] *Am. Chem. J.*, **34**, 357 (1905).

[3] *Ibid.*, **40**, 355 (1908).

[4] *Ibid.*, **42**, 520 (1909).

[5] *Ibid.*, **43**, 187 (1910).

[6] *Ibid.*, **44**, 508 (1910).

[7] *Ibid.*, **46**, 56 (1911).

[8] *Ibid.*, **46**, 240 (1911).

[9] *Ibid.*, **46**, 368 (1911).

[10] *Ibid.*, **48**, 320 (1912).

[11] *Ibid.*, **48**, 411 (1912).

[12] *Ibid.*, **50**, 1 (1913).

[13] *Ibid.*, **48**, 500 (1912).

Shaeffer.[1] Most of the results of these investigations have been recorded in Publication of the Carnegie Institution of Washington, No. 170. For details in connection with the method employed, the above publications must be consulted.

Results.

In the following tables, all conductivities are expressed in Siemen's units, and are molecular conductivities—gram-molecular weights having been used in preparing the solutions. These molecular conductivities (μ_v) were calculated from the equation $\mu_v = Ka\ V/Rb$; where K is the cell constant, V the volume concentration, R the resistance indicated on the rheostat, (*a*) and (*b*) the two arms of the bridge. The percentage dissociation [α] was calculated from the equation $\alpha = 100\mu_v/\mu_\infty$, where μ_∞ is the highest value of μ_v obtained. The temperature coefficients expressed in conductivity units were calculated from the formula

$$\frac{(\mu_v)t_2 - (\mu_v)t_1}{t_2 - t_1} = \text{coefficient},$$

in which $(\mu_v)t_2$ represents the value of μ_v at the higher temperature t_2, and $(\mu_v)t_1$ that at the lower temperature (t_1). These coefficients expressed as percentages were calculated from the formula[2]

$$\frac{(\mu_v)t_2 - (\mu_v)t_1}{t_2 - t_1} \times \frac{100}{(\mu_v)t_1}.$$

For every measurement shown in these tables, three bridge readings involving different values for R were made, and the mean of these readings was taken as the basis of calculation.

Sodium Bromate.—This salt was twice recrystallized and then was dried at 100° for several hours; after cooling over phosphorus pentoxide, the required amount was weighed and put into solution.

TABLE I.

	Molecular conductivity.			Percentage dissociation.		
V.	0°.	15°.	25°.	α 0°.	α 15°.	α 25°.
8	42.77	63.62	78.84	69.9	74.4	74.8
16	44.94	67.03	83.38	73.5	78.4	79.1
32	47.49	70.72	87.95	77.7	82.7	83.5
128	49.64	74.39	92.67	81.2	87.0	88.0
512	52.69	78.76	96.53	86.2	92.1	91.6
1024	53.10	79.59	99.26	86.9	93.1	94.2
2048	58.27	85.45	105.1	95.3	100.0	99.5
4096	61.10	83.34	105.3	100.0	...	100.0

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[1] *Am. Chem. J.*, **49**, 207 (1913).

[2] For the temperature coefficients see *Publ. Carnegie Inst. Wash.*, No. **230** (1915).

Sodium Thiocyanate.—The original solution of this salt was standardized by treating a measured volume with a slight excess of an acidified solution of silver nitrate. The precipitate of silver thiocyanate was filtered into a Gooch crucible, washed and weighed. Duplicate determinations were made as in the case of all solutions standardized by analysis.

TABLE II.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	46.79	69.00	84.36	102.5	80.5	79.8	78.2	78.4
8	49.68	72.57	96.36	107.8	85.5	83.9	89.4	82.5
16	50.96	75.86	94.90	114.2	87.7	87.7	88.0	87.4
32	52.90	79.14	98.81	118.6	91.0	91.4	91.6	90.8
128	55.47	83.19	102.8	124.3	95.4	96.1	95.3	95.1
512	57.77	85.81	106.7	129.7	99.4	99.2	99.0	99.3
1024	57.67	86.50	107.8	130.9	99.4	100.0	100.0	100.0
2048	58.10	86.22	107.8	130.6	100.0	...	...	...

Sodium Thiosulfate.—Iodine which had been resublimed in the presence of potassium iodide was weighed into small flasks with tightly-fitting glass stoppers. About 2 g. of potassium iodide and 0.5 cc. of water had been previously weighed into these flasks. After the weight of the added iodine was determined, the flasks were opened in Erlenmeyer flasks containing 200 cc. of water and potassium iodide. This solution was titrated with the thiosulfate. Starch solution was used as the indicator.

TABLE III.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	77.90	115.3	143.3	172.6	59.2	59.1	58.7	59.4
8	82.52	129.8	160.8	196.0	62.8	66.5	65.9	67.4
16	94.10	143.4	178.4	214.8	71.6	73.5	73.1	73.9
32	103.0	153.2	193.0	235.0	78.4	78.5	79.1	80.8
128	113.1	172.4	214.9	259.9	86.0	88.4	88.0	89.4
512	126.0	189.0	234.0	283.8	95.8	96.9	95.9	97.6
1024	124.8	191.9	239.1	284.1	94.9	98.4	97.9	97.7
2048	128.1	194.1	241.1	284.3	97.5	99.5	98.8	97.8
4096	131.4	195.0	244.0	290.5	100.0	100.0	100.0	100.0

Sodium Dithionate.—After recrystallizing from conductivity water, 10 cc. of the sodium dithionate solution was evaporated to dryness in a weighed platinum dish. After heating to a dull red for some time, the dish and contents were cooled over calcium chloride and weighed. From the weight of the sodium sulfate the strength of the original solution of sodium dithionate was calculated.

TABLE IV.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	91.28	135.9	167.8	202.6	65.6	65.2	64.6	64.4
16	99.71	147.6	183.9	220.3	71.6	70.8	70.8	70.1
32	107.8	161.7	200.5	241.6	77.5	77.6	77.3	76.8
128	121.4	180.9	225.0	272.5	87.2	86.8	86.7	86.7
512	130.6	195.6	242.8	293.9	93.8	93.9	93.6	93.5
1024	137.1	203.6	255.0	308.6	98.6	97.7	98.3	98.1
2048	139.1	208.4	259.4	314.3	100.0	100.0	100.0	100.0
4096	139.1	207.3	258.2	312.7	...	...	...	...

Sodium Pyrophosphate.—This salt was dehydrated and weighed after it had been recrystallized.

TABLE V.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
16	100.2	154.8	194.5	235.3	45.6	44.9	45.3	44.9
32	118.3	181.5	227.5	276.1	53.8	52.6	53.0	52.7
128	159.0	242.7	304.0	370.5	72.3	70.4	70.9	70.8
512	197.0	302.8	384.5	466.7	89.6	87.9	89.7	89.1
1024	211.0	327.0	410.9	508.9	96.0	94.9	95.9	97.2
2048	216.1	336.9	421.8	517.4	98.3	97.7	98.4	98.8
4096	219.7	344.5	428.5	523.4	100.0	100.0	100.0	100.0

Trisodium Phosphate.—All salts of orthophosphoric acid were treated in the same manner. After making a solution of approximately the required strength by weighing the salt, it was standardized by the method of Schmitz.[1] This differs from the usual method, in that the magnesium ammonium phosphate is precipitated in a hot solution, by the slow addition of ammonia to an acid solution of the phosphate, to which an excess of "magnesia mixture" has been previously added. A very pure, coarsely crystalline precipitate, which settles readily, is obtained by this method. From the weight of the magnesium pyrophosphate yielded by this precipitate on ignition, the strength of the solution of the sodium salt was calculated.

TABLE VI.

	Molecular conductivity.			Percentage dissociation.		
V.	0°.	15°.	25°.	α 0°.	α 15°.	α 25°.
32	120.5	195.3	254.2	61.5	63.6	66.8
128	163.7	261.7	338.1	83.6	85.2	88.8
512	185.2	292.8	361.5	94.6	95.3	95.0
1024	195.8	307.0	380.5	100.0	100.0	100.0

Sodium Dihydrogen Phosphate.—The solution of this salt was standardized by the method discussed in connection with trisodium phosphate.

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[1] *Z. anal. Chem.*, 45, 512 (1906).

TABLE VII.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	31.02	47.47	59.79	72.40	72.2	72.4	73.2	71.9
16	33.75	51.62	64.45	79.55	78.5	78.7	78.9	79.0
32	36.16	55.24	69.25	84.25	84.2	84.3	84.8	83.7
128	40.13	60.98	75.39	93.67	93.4	93.0	94.7	93.1
512	43.00	65.52	81.59	99.90	100.0	100.0	100.0	99.3
1024	42.07	64.95	81.17	100.6	...	...	...	100.0

Sodium Tungstate.—The original solution of sodium tungstate was standardized by precipitating the tungstic acid as mercurous tungstate. On ignition this yields the trioxide of tungsten which can be weighed.

TABLE VIII.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	59.56	100.2	...	...	54.8	59.9	...	...
8	69.75	112.7	141.6	172.0	64.2	67.3	66.9	67.3
16	82.65	126.7	159.0	193.2	76.1	75.7	75.2	75.7
32	87.53	134.3	168.7	205.5	80.6	80.3	79.8	80.5
128	98.54	151.5	190.7	233.5	90.7	90.5	90.2	91.4
512	107.25	164.6	207.4	254.1	98.7	98.3	98.1	99.5
1024	108.67	167.3	211.4	255.2	100.0	100.0	100.0	100.0

Sodium Formate.—In a cold *acid* solution, permanganate acts only slowly with formic acid, while in a hot solution the latter is lost by volatilization. In spite of statements to the contrary, oxidation by means of permanganate in an alkaline solution is a most unsatisfactory process. This led to the use of an indirect method of standardization for the sodium formate solution.

An excess of standard permanganate solution was measured from a buret into an alkaline solution of the formate. After standing for some time, a known weight of pure sodium oxalate was added. The solution was then acidified and heated. A standard solution of permanganate was used to titrate this in the usual way. The total amount of permanganate less that which is equivalent to the sodium oxalate is the permanganate used for the oxidation of the sodium formate.

TABLE IX.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	56.09	84.34	105.0	126.4	70.3	71.0	70.9	68.6
8	62.13	91.91	113.6	140.1	77.9	77.4	76.7	76.0
16	64.75	97.82	121.4	147.4	81.2	82.4	81.9	80.0
32	67.72	99.10	130.2	157.1	84.9	83.5	87.9	85.3
128	72.48	109.8	137.7	166.3	90.9	92.5	92.9	90.3
512	74.63	109.6	139.1	166.7	93.6	92.4	93.9	90.5
1024	75.65	112.8	140.9	181.0	94.8	95.0	95.1	98.3
2048	78.68	114.8	147.9	184.7	98.7	96.7	99.8	100.0
4096	79.73	118.7	148.1	184.1	100.0	100.0	100.0	...

Sodium Chromate.—The original solution of this salt was standardized by precipitating the chromium as mercurous chromate by means of a mercurous nitrate solution. On ignition the mercurous chromate leaves a residue of chromic oxide which can be weighed.

TABLE X.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	74.76	113.4	...	...	63.2	64.3	...	...
8	83.56	125.3	156.5	187.9	70.6	71.1	71.3	69.6
16	90.74	137.8	171.3	207.6	76.7	78.2	78.0	76.8
32	98.16	148.6	185.1	224.3	82.9	84.3	84.3	83.0
128	110.40	168.4	206.7	252.2	93.3	95.5	94.2	93.4
512	118.32	176.2	219.5	270.1	100.0	100.0	100.0	100.0
1024	114.60	173.6	216.9	262.3	...	...	...	...

Sodium Dichromate.—The same method of standardization was used in the case of sodium dichromate as was employed with the chromate.

TABLE XI.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	92.18	136.5	...	...	87.2	86.22	..	..
16	96.57	143.5	176.3	211.4	91.3	90.65	90.71	89.88
32	101.25	148.4	182.7	219.5	95.7	93.74	93.98	93.32
128	106.8	158.3	194.7	233.5	100.0	100.0	100.0	100.0
512	106.1	158.3	194.4	234.6	...	...	..	..

Potassium Ferricyanide.—This salt was dried for more than a month over phosphorus pentoxide. The solution was prepared by weighing the required amount of the dry salt and dissolving in the usual manner.

TABLE XII.

	Molecular conductivity.			
V.	0°.	15°.	25°.	35°.
8	158.6	230.2	282.1	...
16	168.8	247.3	303.3	360.1
32	181.4	266.4	326.4	389.3
128	207.4	308.2	380.1	451.7
512	229.2	331.8	410.1	494.5
1024	238.1	354.5	438.9	529.9
2048	244.4	363.0	449.5	543.3
4096	254.5	375.3	465.8	564.3

Ammonium Iodate.—A very dilute solution of the iodate, while cold, was carefully treated with sulfurous acid. When an amount sufficient to discharge the brown color due to free iodine had been added, the solution was warmed until the odor of sulfur dioxide could be detected. The iodine was then determined as silver iodide.

TABLE XIII.

	Molecular conductivity.				Percentage dissociation.			
V	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
16	48.17	72.21	89.97	108.5	85.1	84.88	84.7	84.4
32	50.51	76.35	94.93	114.6	89.2	89.74	89.4	89.1
128	54.34	81.32	101.1	122.2	96.0	95.59	95.2	95.0
512	56.54	85.07	106.2	128.6	99.9	100.0	100.0	100.0
1024	56.60	84.93	105.9	128.0	100.0	...	...	...
2048	55.99	83.92	104.6	127.2	...	...	...	...

Monoammonium Phosphate.—This solution was standardized in the same way as described in connection with sodium phosphate.

TABLE XIV.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	37.56	56.27	69.66	83.53	66.4	67.0	66.5	65.9
8	41.18	61.73	76.50	92.71	72.8	73.5	73.1	73.1
16	44.45	66.55	82.57	99.90	78.6	79.3	78.9	78.8
32	46.72	70.65	87.73	106.48	82.6	84.1	83.8	84.0
128	50.74	76.21	94.89	114.75	89.8	90.8	90.7	90.5
512	53.39	81.01	99.73	121.2	94.5	96.5	95.3	95.6
1024	56.50	83.92	104.6	126.7	100.0	100.0	100.0	100.0

Ammonium Chromate.—The method used for standardization was identical with that used for standardizing the chromate of sodium.

TABLE XV.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	93.63	137.0	...	...	64.7	64.2	...	...
8	102.5	149.8	181.9	215.4	70.8	70.3	69.3	68.8
16	110.5	163.1	199.5	236.7	76.4	76.5	76.0	75.7
32	119.1	176.3	215.4	257.2	82.3	82.7	82.1	82.2
128	135.1	201.2	247.1	292.7	93.4	94.3	94.2	93.6
512	144.6	213.2	262.2	312.7	100.0	100.0	100.0	100.0
1024	143.0	212.6	261.7	312.3	...	...	...	...

Ammonium Thiocyanate.—The amount of thiocyanate present in the original solution was found by weighing the silver thiocyanate formed on treating a portion of the solution with silver nitrate.

TABLE XVI.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	60.46	86.53	106.0	125.7	83.9	82.2	82.0	81.2
8	61.47	89.84	110.3	131.7	85.3	85.3	85.3	85.0
16	63.58	93.60	114.4	137.5	88.3	88.9	88.5	88.8
32	66.30	97.48	119.5	143.4	92.0	92.6	92.5	92.6
128	68.58	101.2	124.2	148.9	95.2	96.2	96.1	96.2
512	71.74	105.2	129.0	154.5	99.6	100.0	99.8	99.8
1024	72.00	105.2	129.2	154.8	100.0	...	100.0	100.0

Lithium Chromate.—The chromate in this solution was determined as it was in the case of sodium chromate.

TABLE XVII.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
8	74.62	112.3	139.9	169.1	65.4	67.3	66.9	67.2
16	82.62	124.1	154.3	187.3	72.4	74.3	73.8	74.5
32	89.83	136.6	169.9	205.5	78.7	81.8	81.3	81.7
128	101.6	155.1	193.0	236.5	89.0	92.9	92.3	94.0
512	106.4	164.5	205.3	249.0	93.2	98.5	98.2	99.0
1024	108.1	166.0	206.2	250.3	94.7	99.4	98.6	99.5
2048	114.1	168.3	209.0	251.4	100.0	100.0	100.0	100.0

Rubidium Iodide.—The iodine was determined as silver iodide.

TABLE XVIII.

	Molecular conductivity.				Percentage dissociation.			
V.	0°.	15°.	25°.	35°.	α 0°.	α 15°.	α 25°.	α 35°.
4	68.40	97.08	...	...	85.41	82.9	...	...
8	70.48	101.4	122.6	145.6	88.0	86.6	85.6	85.2
16	72.59	104.3	127.2	150.6	90.6	89.0	88.8	88.1
32	74.75	108.6	131.7	157.8	93.3	92.7	92.0	92.3
128	78.51	114.2	139.7	166.6	98.0	97.5	97.6	97.5
512	79.92	116.0	142.0	169.5	99.0	99.0	99.2	99.2
1024	80.08	117.1	143.1	170.8	100.0	100.0	100.0	100.0

Discussion of Results.

Conductivities.—Electrical conductivity in solutions of electrolytes depends on the number of ions present and on the velocities of these ions. The velocities will depend upon the size and mass of the ions and upon the viscosity of the medium, other conditions being the same. This leads to the conclusion that a salt showing a high conductivity must be dissociated into a great number of ions, or the ions in solutions must be of such a size that they have a great velocity.

It may be seen from the above tables that certain salts, notably trisodium phosphate, sodium pyrophosphate, ammonium chromate and potassium ferricyanide, show very high conductivity. The first of these compounds is strongly hydrolyzed even at low temperatures. The breaking down of complexes by hydrolysis gives rise to a great number of ions also in the case of the pyrophosphate. It is interesting to compare the conductivity of trisodium phosphate with that of the corresponding potassium compound. While both show very high conductivities at all temperatures, the conductivity of the potassium salt is greater than that of the sodium. We would expect this from the fact that the sodium salt crystallized with twelve molecules of water, indicating great hydration in solution; while the potassium salt has no water of crystallization, which indicates only slightly hydrated ions in solution. The ammonium chromate is somewhat similar to the unhydrated potassium salt mentioned above, in that it carries no water of crystallization, and would therefore be expected to show greater conductivity than the corresponding hydrated salts of sodium and lithium. The high values of μ_v for potassium ferricyanide are largely due to the great number of ions yielded by this compound. The work of Getman and Bassett,[1] conducted in this laboratory, indicates the production of six ions in solutions of this salt. By comparing the conductivities of the chromates of ammonia and the alkali metals, it is found that they stand in the following order:

Potassium chromate > ammonium chromate >
sodium chromate > lithium chromate

Ammonium compounds, as a rule, show higher conductivity than the corresponding potassium salts. This does not seem to be true in the case of the chromates. The smaller conductivity of lithium compounds, when compared with compounds of sodium, is usually attributed to the greater hydration of the lithium ion in solution, as indicated by the greater tendency of lithium salts to crystallize with water. The chromate of lithium, however, crystallizes with one molecule of water, while the chromate of sodium contains ten molecules. The work of Jones and Bassett[2] has shown that many substances have greater hydrating power than is indicated by the water of crystallization contained in them. Such may be the case with lithium chromate.

Rubidium iodide shows a higher conductivity than the iodides of the other alkali metals. Knowing that rubidium has a greater atomic volume than sodium or potassium, we might expect the conductivity to be lowered by a decrease in the velocity of the ions, due to their volume and mass. It should be remembered, however, that the hydrating power of these compounds of the alkali metals decreases with increasing atomic volume. Just as sodium salts are less hydrated than lithium, so rubidium compounds would be expected to hydrate less than potassium. Thus, an apparent exception is explained by the theory of hydration.

Dissociations.—As a means of determining the dissociation of salts in solution, the conductivity method is of great service, but it is far from perfect. Hydrolysis, hydration and polymerization all militate against obtaining a true value for μ_∞. Since most salts show one or more of the above named phenomena, it is certain that dissociations, calculated from conductivity data, are in most cases simply close approximations.

As a rule, salts in aqueous solutions are more dissociated at low temperatures than at high. This is in accord with the Thomson-Nernst hypothesis connecting dissociating power with the dielectric constant of the solvent. Some exceptions to this rule have been found by other investi-

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[1] *Pub. Carnegie Inst. Wash.*, No. 60, 46.

[2] *Am. Chem. J.*, 33, 562 (1905).

gators. Barium nitrate, cadmium iodide, lead nitrate and uranyl acetate have been found to show an increase in dissociation at higher temperatures. Shaeffer[1] has called special attention to the anomalous behavior of tripotassium phosphate, and suggests, as a cause, abnormal exothermic heat of dissociation. A great number of the substances studied in the present investigation showed a slight decrease in dissociation with rise in temperature. Sodium bromate, sodium thiosulfate, trisodium phosphate and lithium chromate showed a well defined increase. Several compounds showed almost identical dissociation at all the temperatures employed.

Temperature Coefficients.[2]

It has been found that the increase in conductivity with rise in temperature is due primarily to the velocity with which the ions move. This velocity is governed by the viscosity of the medium and the volume and mass of the ion. It is well known that the general tendency of rise in temperature is to decrease viscosity, and also the volume and mass of the ion; if the ion is considered not as a charged atom or group of atoms, but as a charged nucleus plus molecules of water which must be carried along in all migrations through the remainder of the solvent. Jones has given a number of proofs for the validity of this conception of ions. He has also shown that these complexes break down at higher temperatures. With these facts in mind, we would expect a greater increase in conductivity with rise in temperature in the case of strongly hydrated salts, than in the case of weakly hydrated substances. Taking the amount of water with which a substance crystallizes as indicative of the extent to which it is hydrated, it is found that all of the compounds referred to in the above tables are in accord with this conception, except potassium ferricyanide and ammonium chromate. Reference has been made to the work of Getman and Bassett, which throws some light on the dissociation of the complex ferricyanide, and also shows that water of crystallization is not always indicative of the degree of hydration to which a compound is subject. While they proved that the ferricyanide is not hydrated, it is rather probable that the lithium chromate is, since lithium salts, as a class, have a much greater tendency to hydrate than the salts of sodium or potassium.

The temperature coefficients expressed in per cent. decrease in every case with rise in temperature. They increase somewhat on dilution. This is especially noticeable with hydrated and hydrolyzed salts.

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[1] *Am. Chem. J.*, 49, 249 (1913).

[2] To save space these coefficients are omitted from this paper. They will be recorded in *Pub. Carnegie Inst. Wash.*, No. 230. Some of the relations between them are here referred to.

Jones[1] has pointed out the following general relations deduced from the study of a large number of data concerning temperature coefficients:

1. Those ions with the largest hydrating power have the largest temperature coefficients of conductivity.

2. Those substances having equal hydrating power have approximately the same temperature coefficients of conductivity.

3. At higher dilutions the temperature coefficients of conductivity, for any given substance, are greater than at lower dilutions.

In the present investigation all of these relations have been found to hold, with the few apparent exceptions which are noted in the above discussion.

Summary.

Eighteen more or less unusual salts were studied with reference to the conductivity, over a range of temperature from 0° to 35°, and, wherever possible, their dissociation has been calculated. Their temperature coefficients were also calculated in two sets of units.

The results of this investigation are, for the most part, in accord with the findings of other workers in this field in this laboratory. Three exceptions to the rule that dissociation decreases with increased temperature were found. Two apparent exceptions to the rule that large temperature coefficients are indicative of great hydration were noted, and possible explanations offered.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

THE VISCOSITIES OF SOLUTIONS OF CAESIUM SALTS IN MIXED SOLVENTS.[2]

BY P. B. DAVIS AND HARRY C. JONES.

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Introduction.

We have endeavored for some time to secure enough caesium salts to study their viscosity in pure and in mixed solvents, but only within the past year have we been successful. Through the courtesy of Professor James Lewis Howe, of Washington and Lee University, a quantity of caesium sulfate was placed at our disposal. This was converted first into the hydroxide, then into the carbonate, and finally into the chloride and nitrate; and with these salts this investigation was carried out.

Caesium is the most electropositive of all the elements, and is further distinguished by possessing the largest atomic volume, being followed in

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[1] *Am. Chem. J.*, **34**, 357 (1905).

[2] This is part of an investigation which was carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones, and the results will be recorded in full in Publication No. 230 of that Institution.